



Sofia Filipe Pereira

Bachelor of Science in Chemical and Biochemical Engineering

Modelling of a wastewater treatment plant using GPS-X

Dissertation to obtain the degree of Master in Chemical and
Biochemical Engineering

Supervisor: Eng. Henrique Figueira, Portucel Soporcel

Co-supervisors: Dr. Adrian Oehmen, FCT-UNL
Prof. Maria Ascensão Reis, FCT-UNL

Jury:

Chairman: Prof. Isabel Coelho, FCT - UNL

Examiner: Dr. António Martins, Águas do Algarve

Member: Eng. Henrique Figueira, Portucel Soporcel



FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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RESUMO

O trabalho presente nesta dissertação foi realizado na empresa Portucel Soporcel, no pólo industrial de Setúbal, e teve como principal objectivo a modelação do processo de tratamento dos efluentes desta indústria, utilizando para o efeito o software GPS-X. Este programa contém uma interface gráfica muito clara e utiliza um tradutor especializado que converte o processo gráfico em equações de balanço mássico, baseadas em modelos dinâmicos. Estes modelos permitem, além da descrição da cinética do processo de tratamento presente na ETAR, simular novos cenários visando o estudo dos parâmetros críticos no processo bem como a optimização e controlo do mesmo.

O efluente que aflui à ETAR da Portucel, proveniente das fábricas de pasta e papel do complexo, é particularmente rico em fibras (sólidos), lenhina, compostos clorados e sulfurados, resinas ácidas, fenóis e amido. Apresenta uma coloração acastanhada, devido à presença de lenhina e tem uma carência química de oxigénio elevada (cerca de $1,095 \text{ g O}_2/\text{m}^3$). A ETAR em estudo utiliza o processo de lamas activadas com arejamento prolongado. Este método permite uma eficiente remoção da carga orgânica ao mesmo tempo que minimiza a produção de lamas.

Para a modelação do processo foi necessária a recolha de dados históricos relativos ao desempenho da ETAR nos últimos 3 anos. Estes dados foram usados como valores de *input* na caracterização do influente e como valores de *output* a atingir na caracterização do efluente tratado. Uma vez que a primeira simulação não conduziu aos resultados de *output* pretendidos, foi necessário proceder à calibração do modelo, através de um estudo mais aprofundado sobre as fracções orgânicas e nutricionais que compõem o influente.

Depois de calibrado o modelo, procedeu-se ao estudo do caudal de ureia. A ureia é adicionada ao influente, antes do início da oxidação biológica, como forma de satisfazer as necessidades de azoto ao longo do processo de tratamento. No entanto, este caudal nunca foi submetido a um estudo que avaliasse, em maior detalhe, as necessidades efectivas deste nutriente. Sendo assim, foram feitas simulações no programa, diminuindo sucessivamente o valor do caudal de ureia e avaliaram-se os resultados obtidos. Por outro lado, procedeu-se também à validação das simulações na própria ETAR da Portucel, reduzindo-se o caudal de ureia adicionado para metade do valor habitual. As simulações e os resultados da Portucel mostraram que, de facto, a adição de ureia não é necessária uma vez que não afecta de forma significativa o processo de tratamento, nomeadamente em termos de remoção de carência química de oxigénio. As simulações mostraram também que a concentração de azoto no efluente final diminui significativamente com a redução do caudal de ureia, o que pode trazer vantagens sob o ponto de vista ambiental.

Palavras – chave: efluentes de pasta e papel, processo de lamas activadas, modelação, calibração, ureia

ABSTRACT

The work present in this thesis was conducted in Portucel Soporcel mill, in the industrial complex of Setúbal, and had as main objective the modelling of the treatment process of the effluents from this industry, using for this purpose the software GPS-X. This program has a clear-cut graphical interface and uses a specialized translator that converts the graphical process into material balance equations, based on dynamic models. These models allow, besides the kinetic description of the treatment process carried out at the WWTP, to simulate new scenarios towards the study of critical parameters for the process as well as optimization and control of the WWTP.

The effluent that arrives to Portucel's WWTP, from the pulp and paper mills of the complex, is particularly rich on fibers (solids), lignin, chlorinated and sulphur compounds, resin acids, phenols and starch. It has a brown colour due to the presence of lignin and has a high oxygen chemical demand (about 1,095 g O₂/m³). The WWTP uses the activated sludge process with extended aeration. This method allows an efficient removal of organics at the same time as it minimizes the sludge production.

For the modelling of the process it was necessary to collect historical data related to the WWTP's performance over the last 3 years. This data was used as input values for the influent characterisation and as output values to achieve the treated effluent characterisation. Since the first simulation did not lead to the desired output results, it was necessary to proceed to the model calibration, by means of a more detailed study concerning the nutrient and organic fractions of the influent.

Once the model was calibrated, a study of the urea flowrate was conducted. The urea is added to the influent, before the beginning of the biological oxidation, as a way to satisfy the nitrogen requirements along the treatment process. However, this flowrate was never submitted to a study that evaluated, in a higher detail, the effective requirements of this nutrient. Thus, some simulations were done using the software, by decreasing successively the value of the urea flowrate and the results obtained were analyzed. Furthermore, these simulations were validated in the WWTP itself, at Portucel, through the decrease of the urea flowrate to half the normal value. Both the simulations and Portucel's results showed that, actually, the addition of urea is not necessary because it does not affect the treatment process in a significant way, namely in terms of the removal of chemical oxygen demand. The simulations have also showed that the concentration of nitrogen in the final effluent diminishes significantly with the reduction of the urea flowrate, which could be advantageous in an environmental point of view.

Keywords: pulp and paper effluents, activated sludge process, modelling, calibration, urea

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ABBREVIATIONS AND SYMBOLS

AOX - Adsorbable Organic Halides
ASM – Activated Sludge Model
bCOD – Biodegradable COD
BOD – Biochemical Oxygen Demand
BOD₅ – Biochemical Oxygen Demand in a 5 day incubation period
C₅H₇NO₂ – Biomass (chemical formula)
CaCO₃ – Calcium Carbonate
CO₂ – Carbon Dioxide
COD – Chemical Oxygen Demand
DO – Dissolved Oxygen
F/M – Food to Microorganism ratio
H⁺ - Hydrogen ion
H₂O – Water
MLSS – Mixed Liquor Suspended Solids
N – Nitrogen
N₂ – Dinitrogen
NH₄⁺ - Ammonia
NO₂⁻ - Nitrite
NO₃⁻ - Nitrate
nbCOD – Nonbiodegradable COD
O₂ – Oxygen molecule
P – Phosphorus
PAO – Polyphosphate Accumulating Organisms
PHA – Poly-hydroxy-alkanoates
rbCOD – Readily Biodegradable COD
sbCOD – Slowly Biodegradable COD
SO₂⁻ - Sulphur Dioxide
SO₃⁻ - Sulphur Trioxide
SRT – Solids Retention Time
SVI – Sludge Volume Index
TKN – Total Kjeldahl Nitrogen
TN – Total Nitrogen
TP – Total Phosphorus
TSS – Total Suspended Solids
VSS – Volatile Suspended Solids
WWTP – Wastewater Treatment Plant
(w/w) – weight/weight

Part I

State of the art

CHAPTER 1. INTRODUCTION

1.1 GENERAL CONTEXT

Pulp and paper industry is one of the largest polluting industries. The effluent of a pulp and paper mill contains an abundance of different substances, both organic and inorganic. The particulate material is mainly made up of wood fibres while soluble pollutants become part of the wastewater through different rejected flows from purification and separation processes within the pulp and paper mill. They consist mainly of lignin, carbohydrates, extractives and their degradation products. Different additives and chemicals may also be found as soluble components in the wastewater. The major contribution of additives is starch, which is added to increase the strength of the paper [1].

If these wastewaters are not efficiently treated, the large amounts of organic matter and nutrients present in the effluent will lead to severe impacts on the aquatic ecosystem, such as eutrophication and the release of toxic pollutants (chlorinated compounds, resin acids, phenols). The most frequent way to reduce organic matter in the effluents of pulp and paper mills is by biological oxidation processes such as the activated sludge process. This method depends upon groups of microorganisms, mainly bacteria, along with protozoan, fungi and rotifers, being maintained in contact with the organic matter in the waste in an aerobic environment. This allows the reduction of the organic load with a minimum sludge production [2].

An activated sludge process is a complex system in which a range of bacterial conversion and transport processes occur. Kinetics, stoichiometry and transport processes play an important role in the conversion of contaminants. Mathematical models are needed for quantitative evaluation and optimization of the processes. Presently, there has been a strong demand for the application of mathematical models for biological treatment processes simulation, in full-scale WWTPs. Models allow to evaluate not only the system's dynamics but also engineering questions (WWTP optimization and control), minimizing the costs associated with laboratory analysis. However, the application of a model to describe a WWTP demands some careful study, parameterization and calibration. Nowadays there are many commercial softwares available that offer a variety of choices in terms of biological processes modelling [3].

1.2 MOTIVATION

The main aim of this study is the application of one of the state-of-the-art modelling softwares to describe the behaviour of the WWTP of Portucel, a pulp and paper mill located in Setúbal. In particular, this study focuses on the tasks of influent characterisation and model calibration with the purpose of building a model that explains the particularities of this type of effluent in terms of components characterisation and how they behave in the biological treatment. Moreover, it is also an objective of this study to analyse the influence of the urea addition on the treated effluent and sludge production rate.

1.3 OUTLINE OF WORK

Chapter 2 introduces the basic concepts of the pulp and paper industry, addressing the process of pulp and paper making, the origin and composition of the effluents and the usual approach to treat them – the activated sludge process. This process is described in more detail, attending to issues such as biochemical components and biological reactions that occur in a wastewater treatment plant (WWTP) and its physical characterisation and control parameters.

In Chapter 3 the concept of modelling is presented, as well as a state-of-the-art concerning this topic. The model used to describe the behaviour of the WWTP, ASM2d, is explained in terms of components and kinetics of the involved biological processes.

Chapter 4 refers to the modelling of Portucel's WWTP. The chapter begins with an explanation of the approach used for modelling, followed by a description of Portucel's WWTP, as well as the data collection of the main parameters. Then, the step of influent characterisation during model calibration is described. Lastly, a case study is presented (Chapter 5), concerning the effect of the decrease in urea flowrate on the treatment process.

Chapter 6 addresses the conclusions and future developments of this study.

CHAPTER 2. GENERAL CONCEPTS

2.1 PULP AND PAPER INDUSTRY

Paper is a product widely used in our society and it can be found in various forms. It is essentially a sheet of cellulose fibres with a number of supplements, added to affect the paper's quality and fitness for intended end use. Historical records report that paper was invented in 150 AD, by the Chinese Emperor Ts'ai Lun, made from a suspension of hemp waste in water, washed, soaked, and beaten to a pulp with a wooden mallet. From China, papermaking moved to Korea and to the west, via the Silk Road. Pulp was initially prepared from the fibers of hemp, mulberry, bamboo, rice straw, and cloth. It was only in 1850 that wood was first used for making pulp. Due to a rag shortage, along with increasing demand for paper, European and American inventors searched for alternative supplies for making pulp. These inventors found mechanical and chemical methods for efficiently making paper from wood. The first species of trees used for paper making were pine and spruce from the coniferous forests of Europe and North America. Then, hardwood species such as eucalyptus, birch, aspen and maple were introduced, mostly motivated by lower costs and better availability [4].

Pulp and paper mills may exist separately or as integrated operations. An integrated paper mill is one that conducts pulp manufacturing on-site. Pulp can be produced by mechanical or chemical methods. In mechanical pulping the wood is pressed against a grinder which destroys the wood matrix separating the fibers from each other. This type of pulping maintains the main part of the lignin, achieving high yield ($\approx 95\%$) with tolerable strength properties and brightness. However, it is associated with a low resistance to aging which results in a tendency to discolour. This method is used for weaker paper materials such as newspapers, paperbacked books and magazines. Chemical pulping removes non cellulose wood components leaving intact the cellulose fibers through the cooking of raw materials with a solution of chemicals under elevated pressure, using the kraft (sulphate), sulphite or soda processes. Chemical pulping yields approximately 50% but offers higher strength properties and the fibers are more easily bleached. This type of pulping is used on most papers produced commercially in the world today [5].

For what concerns the chemical pulping processes, the sulphate (kraft) and sulphite processes are the most important ones. The difference between them lies on the different chemicals used to attack and remove lignin. Sulphite pulping involves the use of sulphur dioxide adsorbed in a base solution. It can be carried out at different pH levels with different bases. In contrast, kraft pulping is a distinctly alkaline process and works in the range of pH of 11 - 14, using as cooking chemicals sodium hydroxide and sodium sulphide. The sulphate process is

the currently dominating chemical pulping process worldwide because it is related to superior pulp strength, is applicable to all wood species and has an efficient chemical recovery system. However, the chemistry associated with this process has an intrinsic potential trouble of malodorous compounds [6] [7].

In terms of operational steps, kraft pulping begins with wood chipping, debarking and screening. After a pre-impregnation step the wood chips are “cooked” in a digester under high pressure and temperature in the presence of white liquor, a water solution of sodium sulphide and sodium hydroxide. This mixture dissolves most of the lignin and only some of the hemicelluloses, leaving mostly cellulose to hold the fibers together. Subsequent to the digestion the wood pulp is washed and screened in order to remove knots that were not completely broken down in the digester. The spent cooking liquor, containing process chemicals, water and chemicals from the wood, is combined with pulp wash water to form the black liquor. The latter is sent to the chemical recovery process in order to recuperate chemicals and heat. The black liquor is concentrated through evaporation and combusted in a recovery furnace, where heat from the combustion of organics is recovered for process use and for the generation of electrical power. To compensate for chemicals that are lost in the pulp mill cycle, sodium and sulphur chemicals are added to the black liquor before combustion. Traditionally, sodium sulphate was the normal 'make-up' chemical, supplying both sodium and sulphur. However, modern mills only lose small amounts of sulphur and it has become necessary to partially use 'sulphur free' make-up chemicals, in form of sodium carbonate. The inorganic chemicals are recovered as molten smelt. Water and quicklime are used to convert this smelt back to white liquor in a causticising tank. The lime mud that precipitates from the tank is calcined in a lime kiln to regenerate quicklime. [8]

Bleaching of the pulp is carried out in various stages, usually four to five, each stage being conducted in a different tower, with different chemicals. Firstly the pulp is treated with sodium hydroxide (NaOH) in the presence of oxygen (O_2) – a delignification step. The NaOH removes hydrogen ions from the lignin and the O_2 breaks down the polymer. Then the pulp is treated in other stages, called extraction stages. They involved treatment with chlorine dioxide (ClO_2), a mixture of NaOH, O_2 and peroxide and finally with ClO_2 again to remove the remaining lignin. The resulting pulp can be dried and stored for external sale or it can be directly pumped to a close paper mill in the case of integrated pulp and paper mills [8].

Paper making is the process where pulp fibres are mechanically and chemically treated: the dilute pulp suspension is spread over a mesh surface, the water is removed by suction, and the resulting pad of cellulose fibres is pressed and dried to form paper. During the process various chemicals are added in order to give water resistance, increase strength and produce coloured paper or also to serve as inorganic filters. [9]

In Portugal, the group Portucel Soporcel is the leader in the pulp and paper industry. It is the main producer of UWF¹ paper and BEKP² pulp in Europe, with a total of 1.6 Mton/year of UWF paper and 1.4 Mton/year of BEKP pulp. In 2013, it was the second largest national exporter with an income of 1.2 billion Euros. The group is the main national producer of energy obtained through biomass cogeneration and achieves a surplus in terms of electrical energy, producing about 2.5 TWh/year. They have strong sociological and cultural values, investing in sustainability and biodiversity conservation. The industrial complexes are located in Cacia, Figueira da Foz and Setúbal. The first mill stands at the heart of Portugal's largest area of eucalyptus forest and produces about 285 thousand tons/year of pulp designed for special applications; the mill of Figueira da Foz involves the integrated pulp and paper mill with an annual production of 800 thousand tons of UWF paper; the mill of Setúbal comprises a pulp mill and two paper mills. This complex is one of the largest and most advanced in Southern Europe. Its competitive advantages include excellent energy performance and eco-efficiency. The group's paper grades include Navigator, Pioneer, Inacopia, Explorer, Discovery, Soporset and many more [10].



Figure 1 – Portucel pulp and paper mill in Setúbal: (a) outside view of the pulp mill; (b) inside view of the paper mill. Source: Portucel Soporcel group [10]

¹ UWF - Uncoated Wood Free Printing and Writing Paper

² BEKP – Bleached Eucalyptus Kraft Pulp

2.2 PULP AND PAPER EFFLUENTS

Pulp and paper is the sixth largest polluter industry, preceded by oil, cement, leather, textile and steel industries. In a pulp mill about 50% of the raw materials leave the process as gaseous, solid and liquid waste. According to Muna Ali and T.R. Sreekrishan, pulp and paper waste can be classified into four main categories (Table 1):

Table 1- Classification of pulp and paper waste. Adapted from: Muna Ali and T.R. Sreekrishan [11]

Type of waste:	Composition and source:
Gases	<ul style="list-style-type: none">• Malodorous gases such as hydrogen sulphide and mercaptan;• Oxides of sulphur such as SO₂ and SO₃
Effluents	<ul style="list-style-type: none">• Suspended solids including bark particles, fiber pigments and dirt;• Dissolved colloidal organics such as hemicelluloses, sugars, sizing agents;• Chromatophores - mainly lignin compounds;• Chlorinated compounds;• Dissolved inorganics such as NaOH and Na₂SO₄.
Particulates	<ul style="list-style-type: none">• Fly ash from coal;• Char.
Solids	<ul style="list-style-type: none">• Sludges from primary and secondary treatment and recovery section;• Solids such as grit, bark and other mill wastes.

Effluents are a major concern in a pulp and paper mill, since this industry consumes a large amount of water - the consumption of water in the processes of cooking and bleaching can reach a total of 200 m³ water/ton pulp produced. The resulting wastewater carries with it a considerable amount of pollutants such as chlorinated compounds (as adsorbable organic halides – AOX), suspended solids, lignin, sulphur compounds, etc. While some of these pollutants are naturally occurring wood extractives (tannins, resin acids, stilbenes, lignin), others are xenobiotic compounds that are formed during the process of pulping and paper making (chlorinated lignin, resin acids and phenols). Chlorinated organic compounds may include dioxins and furans that are recalcitrant to degradation and tend to persist in nature [12].

These effluents cause considerable damage to the receiving waters if discharged untreated since they have a high biochemical demand (BOD) and chemical oxygen demand (COD). The BOD parameter measures the quantity of oxygen necessary to stabilize, biologically, the

organic matter and the COD parameter encompasses the majority of organic compounds and oxidizable minerals such as sulphides and sulphites, which are susceptible of being oxidized by potassium dichromate in an acidified medium.

Also, the effluents that result from the pulp making process are characterized by the presence of an intense colour, which comes from the lignin. The colour causes not only a serious aesthetic problem, but also a negative effect in the algae and aquatic plant productivity [13]. The main effluent discharges and pollutant effects for each process unit are described below:

- **Pulp mill**

Table 2- Discharge of organic substances from kraft pulp mills. Source: European Commission [14]

Process stage	COD (kg/ADt³)
Wood handling	1 – 10
Condensates	2 – 8
Spillages	7 - 10
Washing loss	6 – 12
Bleaching	15 – 65
Total	31 – 105

Debarking consumes water and creates an effluent containing nutrients, fibres and oxygen-consuming organic compounds such as resin acids and fatty acids. Condensates derive from the process vapours from digesters and the evaporation plants. The COD is mainly methanol with some ethanol and a number of organic sulphuric compounds, turpentine and inorganic nitrous compounds. They may also contain ketones, terpenes, phenolics as well as various dissolved gases. A large proportion of nitrogen discharged from a kraft pulp mill is contained in condensates. Spillage of fibres and black liquor takes place in the digestion, screening and evaporation plants, washing and also from tanks. Spillage of white liquor, weak liquor and lime occurs during causticizing. The washing losses are mainly black liquor residues from the handling of unbleached pulp. As can be seen in Table 2, the bleach plant is the most important point of pollutants discharge to water in a pulp mill. The emissions from the bleach plant depend on the degree of delignification, the bleaching sequences/steps, the chemicals used and the type of wood. For what concerns the nutrients, they originate mainly from the wood itself. Nitrogen discharges derive mainly from the unbleached part of the process, whereas phosphorus discharges come from the bleachery [14] [15].

³ ADt – Air Dry ton of pulp

- **Paper mill**

In paper mills, water is mainly used as cleaning water for the paper machine (shower water) and as a solvent for fillers and additives. There are a large number of chemical additives that can be used in papermaking. The choice depends on the type of paper wanted: for the production of the bulk grades such as packaging papers, some printing and writing papers, newsprint and hygienic papers the use of chemicals is limited to about 10 to 20 different groups of additives. For production of fine papers and especially of speciality papers, a much higher number of chemicals may be used. The discharge of additives to water is directly related to the power of retention of the chemical additives: the higher the retention the less chemical additives pass to the wastewater [14]

The main sources of wastewater discharges from paper mills are:

- Rejects from stock cleaning - The rejects from the paper machine contain impurities such as sand and also some valuable fibres, suspended in water.
- Excess white water - the process water that results from the paper machine and spent shower water from the cleaning of wires and felts. The main part of this water is recycled within the paper machine as dilution water and shower water, while the excess is discharged to the effluent. It generally passes through a fibre recovery unit before being discharged.
- Temporary and accidental discharges

Table 3 - Typical wastewater discharges from paper mills. Adapted from: European Comission [14]

Paper type	COD (kg/t)	BOD₅⁴(kg/t)
Wood free printing and writing	7 – 15	4 – 8
Paper board	5 – 15	3 – 7
Tissue	8 – 15	5 – 7
Total	20 - 45	12 - 22

The discharge of organic matter has two main sources: 1) organic matter included in the pulp and 2) organic chemicals applied as additives or auxiliaries in papermaking, which are not retained in the paper web. Starch and their degradation products contribute significantly to the organic load. Some chemical additives may also contain organic bounded nitrogen compounds, for example the optical brighteners - contain up to 30% organic bound nitrogen (urea) [14].

⁴ BOD₅ – Biochemical oxygen demand for a period of incubation of 5 days.

2.3 ACTIVATED SLUDGE PROCESS

Description:

Activated sludge refers to a mass of microorganisms cultivated in the treatment course with the purpose of transforming organic matter into carbon dioxide, water, and other inorganic compounds. This concept was developed around 1913 at the Lawrence Experiment Station in Massachusetts by Clark and Gage and by Arden and Lockett, in 1914, at the Manchester Sewage Works. They studied the aeration of wastewater in tanks and the hastening of the oxidation of organic matter and found out that sludge played an important role in the reduction of pollutants. This process is now widely used for biological treatment of municipal and industrial wastewaters and is very popular in the treatment of pulp and paper effluents. The main purpose of this method is to achieve the maximum organic load reduction with a minimum sludge production [16].

The activated sludge process contains the following unit processes (see Figure 4) [16]:

- An aeration tank, known as biological reactor, where the microorganisms growth aerobically and suspended in the wastewater, degrading the organic matter. This growing mass of microorganisms is called mixed liquor volatile suspended solids (MLVSS);
- A solid-liquid separation step, normally consisting of a clarification process. An important characteristic of the activated-sludge process is the formation of floc particles, ranging in size from 50 μm to 200 μm , which can be removed by gravity settling, leaving a relatively clear liquid as the treated effluent. The overflow (liquid phase) relates to the treated effluent and the solid phase relates to the biological sludge;
- A system of sludge recirculation that takes place from the bottom of the clarifiers back to the aeration tank in order to guarantee an adequate concentration of microorganisms inside the biological reactor;
- A system of sludge extraction (purge) that conveys the excess sludge to a sludge treatment line, avoiding an excessive increase of the microorganisms concentration inside the biological reactor.

The activated sludge process is normally preceded by a primary sedimentation. This operation is responsible for the removal of the majority of the settleable solids, whereas the biological process is most appropriate for removal of soluble, colloidal and particulate organic matter and also for the biological processes of nitrification, denitrification and phosphorus

removal. The microorganisms are maintained in liquid suspension through a system of mechanical or diffused aeration. The aeration system must be adequate not only for keeping the microorganisms in suspension but also to satisfy the oxygen needs for growth and endogenous respiration of biomass and also for nitrification. Therefore the minimum dissolved oxygen (DO) in the aeration tank must be kept at approximately 2 mg O₂/L. For the removal of phosphorus and for denitrification, anaerobic and anoxic zones are also necessary in addition to the aerobic zone [16].

Components and organisms involved:

To understand the chemical reactions and biological processes that occur in a WWTP treated with the activated sludge process one must have knowledge about the components that serve as substrate and the ones that are biologically inert. For that matter, a COD classification is given, according to the degree of biodegradability of the organic matter [16] [17]:

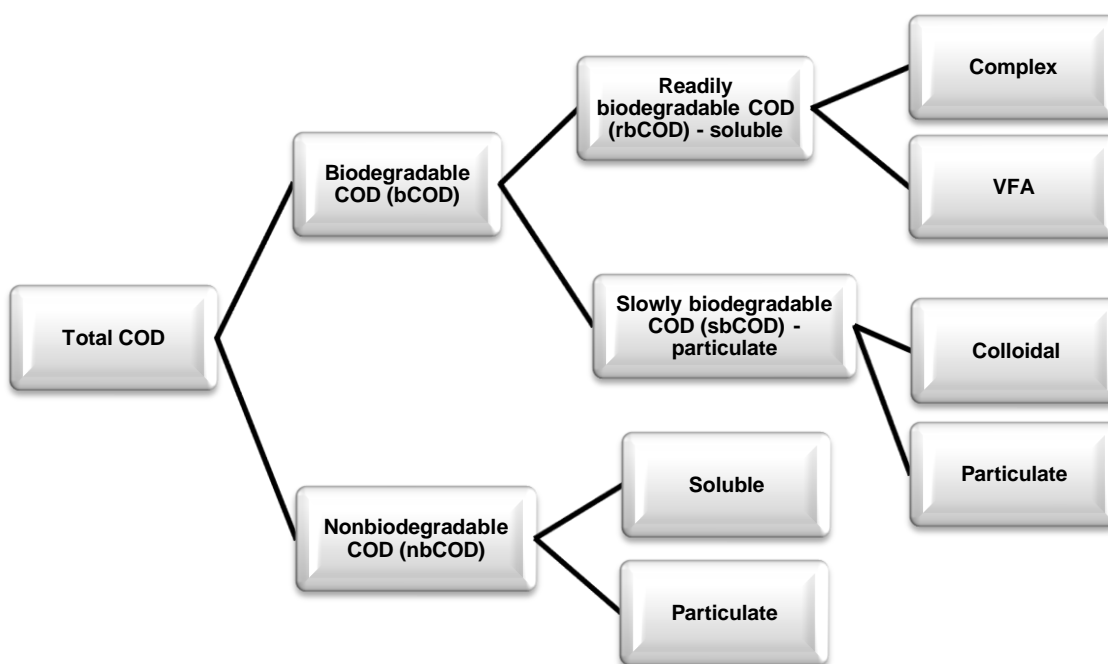


Figure 2 - Classification of the Chemical Oxygen Demand according to biodegradability. Source: Eckenfelder and Grau [17]

Unlike BOD, some portion of the COD is not biodegradable and thus COD is divided into biodegradable (bCOD) and nonbiodegradable fractions (nbCOD). Each of these fractions can be splitted according to the physical state of the matter: soluble or particulate. The nonbiodegradable soluble COD will be found in the treated effluent and the particulate contributes to the total sludge production. Concerning the biodegradable COD, the soluble portion – readily biodegradable COD (rbCOD) is rapidly assimilated by the biomass while the particulate and colloidal COD (sbCOD) must first be hydrolysed by extracellular enzymes to be available for assimilation. Furthermore, rbCOD can be converted to acetate through fermentation, in anaerobic conditions, for uptake by the phosphorus-storing bacteria [16] [17].

In terms of microorganisms, the activated sludge process consists of mixed microbial communities with a wide variety of organisms, including bacteria, protozoa, fungi, rotifers and possibly algae. These are classified according to the carbon and energy sources. For what concerns carbon sources, organisms obtain their carbon for cell growth from either organic matter (heterotrophs) or carbon dioxide (autotrophs). The energy needed for cell synthesis may be supplied by light (phototrophs) or by chemical oxidation reaction (chemotrophs). An example of phototrophic organisms is algae and/or sulphur-reducing bacteria. Chemotrophs may be either heterotrophic (protozoa, fungi and most bacteria) or autotrophic (nitrifying bacteria). Chemoautotrophs obtain energy from the oxidation of reduced inorganic compounds such as ammonia, nitrate, ferrous iron and sulphide while chemoheterotrophs derive their energy from the oxidation of organic compounds. When oxygen is used as the electron acceptor the reaction is termed aerobic and therefore, reactions involving other electron acceptors are considered anaerobic. The term anoxic is used to distinguish the use of nitrite or nitrate for electron acceptors from the others, under anaerobic conditions. Under anoxic conditions nitrite or nitrate are reduced to gaseous nitrogen in a process known as denitrification [16] [17].

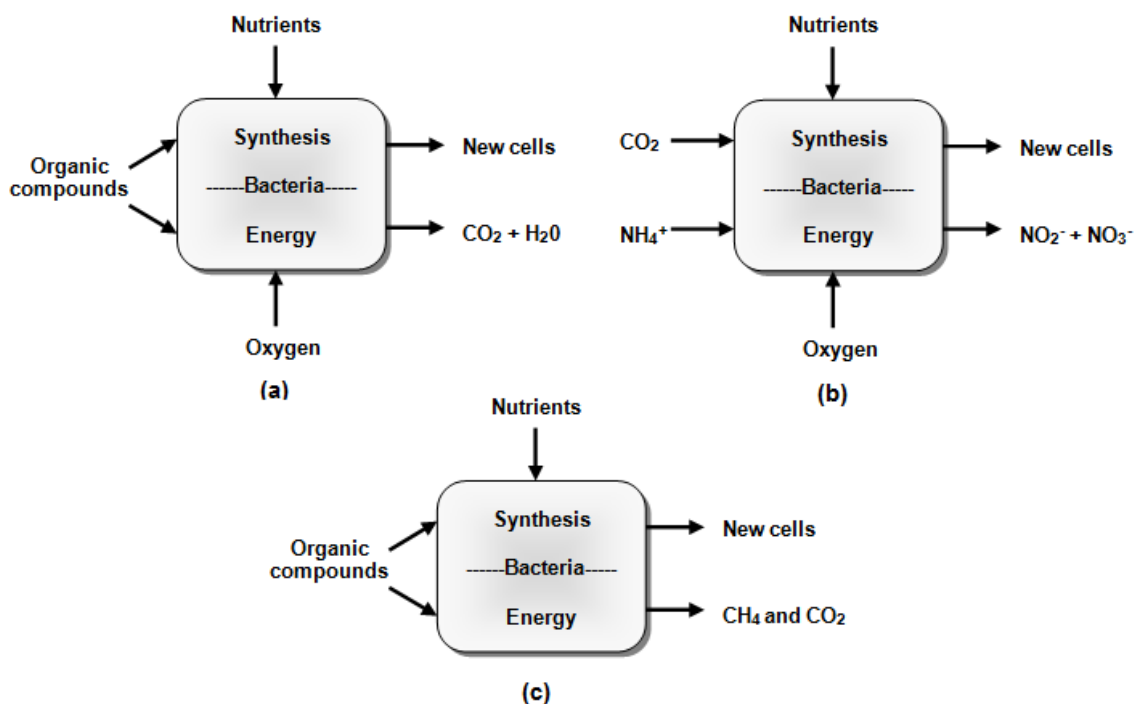


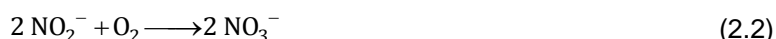
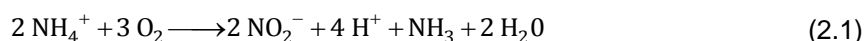
Figure 3 - Bacteria metabolism: (a) aerobic, heterotrophic; (b) aerobic, autotrophic; (c) anaerobic, heterotrophic. Adapted from: Metcalf and Eddy [16]

In short, the biological reactions concerning the removal/formation of organic matter are listed below [16]:

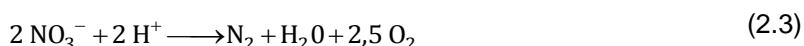
Table 4 - Biological processes concerning organic matter.

<pre> graph TD A[Slowly biodegr. matter] -- Hydrolysis --> B[Readily biodegr. matter] B -- Biological growth --> C[Biomass] C -- Decay --> D[Inert Material] D -- Feedback --> A </pre>	Hydrolysis:
	Extracellular biological reaction where hydrolytic enzymes break down large organic molecules into smaller ones that can pass through the bacterial cell wall.
	Biological growth (aerobic heterotrophics):
	$\begin{matrix} \text{COHNS} \\ \text{Organic matter} \end{matrix} + \text{O}_2 + \text{nutrients} \xrightarrow{\text{bacteria}} \text{CO}_2 + \text{NH}_3 + \text{C}_5\text{H}_7\text{NO}_2 + \text{other end products}$
	Endogenous respiration:
	<p>Bacteria use their own storage pools of organic matter for maintenance purposes. In this process, energy is provided by the oxidation of the organic matter contained in biomass, which leads to undegradable matter and nutrients release.</p> $\text{C}_5\text{H}_7\text{NO}_2 + 5 \text{O}_2 \xrightarrow{\text{bacteria}} 5 \text{CO}_2 + 2 \text{H}_2\text{O} + \text{NH}_3 + \text{energy}$
	Lysis/Decay:
	The depletion of substrate and/or nutrients and the subsequent accumulation of metabolic waste products lead to the decay of microorganisms.

Autotrophic organisms oxidize ammonia to produce the required energy for CO₂ uptake and growth - this process is named nitrification. The need for nitrification in a wastewater treatment concerns the necessity of nitrogen removal in order to control eutrophication. This process is a two-step oxidation: in the first step, nitroso-bacteria oxidize ammonia to nitrite and in the second step the nitro-bacteria oxidize nitrite to nitrate [18]:



In the denitrification process nitrate is reduced to nitrogen and other gaseous end products. Nitrification is an aerobic process while the denitrification is an anoxic process and therefore it implies the existence of an anoxic zone in the biological reactor [18].



Similarly to nitrogen, the need of phosphorus removal is also associated with the intention of avoiding eutrophication in the effluent discharge to the aquatic system. Phosphate may be present in the wastewater on the form of ortho-phosphate (PO_4^{3-}), polyphosphate (P_2O_7) and/or organic phosphate. The biological removal of this nutrient is carried by a certain group of microorganisms, called PAOs – polyphosphate accumulating organisms. These organisms have a specific metabolism, according to the anaerobic or aerobic conditions [16] [18]:

- Under anaerobic conditions, PAOs assimilate fermentation products (volatile fatty acids such as acetate) and store them as poly-hydroxy-alkanoates (PHA) within the cells with the simultaneous glycogen and polyphosphate consumption – phosphate release.
- Under aerobic conditions, PAOs uptake phosphate and form glycogen, restoring the pools of polyphosphate and glycogen. In this step energy is produced by the consumption of PHA resulting in the growth of PAOs.

Phosphorus can be incorporated into either biological solids (e.g. PAOs) or chemical precipitates. In a pulp WWTP, the phosphate precipitation with calcium is very frequent, due to the elevated concentration of this metal in the wastewater [16].

Physical Characterisation:

The following figure shows a scheme of the activated sludge process:

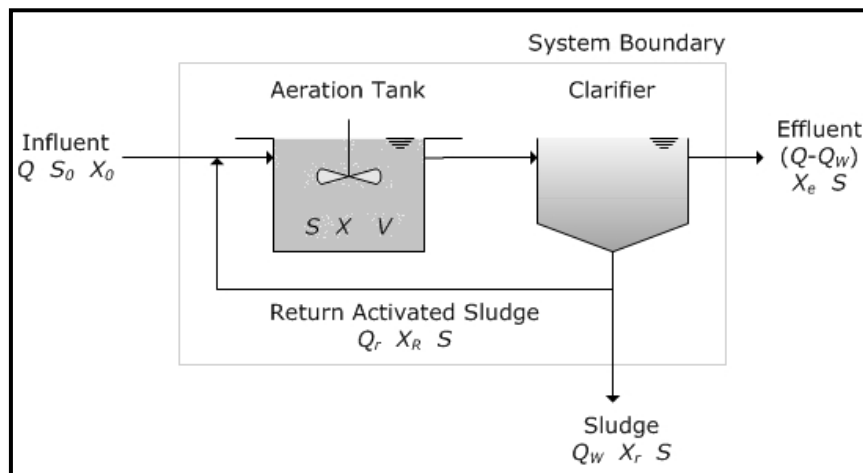


Figure 4 - Schematic diagram of Activated Sludge Process. Adapted from: Lenntech [19]

Where:

- Q – influent flowrate (m^3/d);
- Q_r – sludge recirculation flowrate (m^3/d);
- Q_w – excess sludge flowrate (m^3/d);
- S_0 – influent soluble substrate concentration ($\text{g BOD}/\text{m}^3$) or ($\text{g bCOD}/\text{m}^3$);
- S – effluent soluble substrate concentration ($\text{g BOD}/\text{m}^3$) or ($\text{g bCOD}/\text{m}^3$);

- X_0 – concentration of biomass in influent (g VSS⁵/m³);
- X – biomass concentration (g VSS/m³);
- X_R – concentration of biomass in the return line from clarifier (g VSS/m³);
- X_r – concentration of biomass in the excess sludge drain (g VSS/m³);
- X_e – concentration of biomass in the effluent (g VSS/m³);
- V – volume of the aeration tank (m³)

Writing a biomass balance for the system:

$$\text{Accumulation} = \text{inflow} - \text{outflow} + \text{net growth} \quad (2.4)$$

$$\Leftrightarrow \frac{dX}{dt} V = Q \times X_0 - [(Q - Q_W) X_e + Q_W X_R] + r_g \times V \quad (2.5)$$

With r_g being the net rate of biomass production (g VSS/m³.d). If it is assumed that the concentration of microorganisms in the influent can be neglected and that steady-state conditions prevails $\left(\frac{dX}{dt} = 0\right)$ the equation can be simplified to:

$$\Leftrightarrow (Q - Q_W) X_e + Q_W X_R = r_g \times V \quad (2.6)$$

Dividing the equation by $V \times X$:

$$\Leftrightarrow \frac{(Q - Q_W) X_e + Q_W X_R}{V \times X} = \frac{r_g}{X} \quad (2.7)$$

Taking into account the definition of net biomass production rate:

$$r_g = -Y \times r_{su} - k_d \times X \quad (2.8)$$

$$\Leftrightarrow \frac{(Q - Q_W) X_e + Q_W X_R}{V \times X} = -Y \times \frac{r_{su}}{X} - k_d \quad (2.9)$$

With Y being the synthesis yield coefficient (g VSS/g bCOD), r_{su} the rate of substrate utilization (g bCOD/(m³.d)) and k_d the endogenous decay rate coefficient (d⁻¹). The inverse of the right-hand term is defined as the average solids retention time (SRT) and thus:

$$\Leftrightarrow \text{SRT} = \frac{V \times X}{(Q - Q_W) X_e + Q_W X_R} \quad (2.10)$$

The solids retention time, also known as sludge age, is defined as the average time in days the suspended solids remain in the entire system. The SRT is a particularly important parameter in activated sludge processes as it gives an indication of the plant's biological state: carbon removal, nitrification and condition of biomass (settleability). The common range for sludge age for a conventional activated sludge plant is between 3 to 15 days. For extended aeration

⁵ VSS – Volatile Suspended Solids

activated sludge plants the range is between about 15 and 30 days. This parameter can be controlled by adjusting the rate of activated sludge wasted from the system [20].

The food to microorganism (F/M) ratio is a parameter that describes the degree of starvation of the microorganisms. It is defined as the rate of BOD or COD applied per unit volume of mixed liquor:

$$\frac{F}{M} = \frac{Q \times S_0}{V \times X} \quad (2.11)$$

If the F/M ratio has a high value (high load) it means that the quantity of available substrate is high and therefore the microorganisms grow quickly and the majority of them are purged through the sludge. On the other hand, if there is a higher number of microorganisms than available substrate (low F/M) the growth will be much lower. Microorganisms will use the oxygen to metabolize the stored substrate (endogenous respiration) and as a consequence they produce less and better settling sludge. The F/M ratio in a conventional activated sludge plant conducted with extended aeration ranges between 0.05 and 0.15 [20].

The Sludge Volume Index (SVI) is the parameter used to evaluate the settleability and compactibility of sludge. This parameter is determined by placing a mixed liquor sample in a 1 to 2 liters cylinder and measuring the settled volume after 30 minutes and the corresponding MLSS concentration.

$$SVI = \frac{(\text{settled volume of sludge, mL/L}) \times (10^3 \text{ mg/g})}{(\text{suspended solids, mg/L})} = \text{mL/g} \quad (2.12)$$

The common range for an SVI at a conventional activated sludge plant should be between 50 and 150. A superior value is associated to the excessive growth of filamentous bacteria – bulking. The filamentous bacteria tend to grow in long strands, having much greater volume and surface area than conventional floc and as a result they are very slow to settle, damaging the performance of the clarification. Bulking problems are associated with a low DO and low F/M and it can be detected because it is associated with high SVI values. The solutions for this problem involve the increasing of the recirculation and excess sludge flowrates and increasing of the DO in the aeration tank [20] [21].

In terms of hydraulic configuration, the biological reactor is normally a completely-mixed activated sludge reactor (CMAS), plug-flow reactor (PFR) or a sequencing batch reactor (SBR). In a CMAS reactor it is assumed that the mixture of the influent and recirculated sludge occurs instantaneously and therefore the distribution of the substrate load, mixed liquor volatile suspended solids (MLSS), as long as the oxygen requirements are uniform along the reactor. Although it is easy to operate, the low quantity of available substrate (low F/M ratio) tends to enhance the arising of filamentous bacteria, associated with bulking problems. This type of reactor is also associated with large volumes and dilution rates, which is why this configuration is the most suitable for dealing with toxic pollutants [22].

In a PFR there is no dispersion of the influent, it flows along the reactor with a minimum longitudinal mixture (in ideal conditions) leaving in the same sequence that it entered. This configuration diminishes the probability of bulking problems, since the gradient of concentration of dissolved particles is lower and as a result the growth of filamentous bacteria is more limited. The SBR is the most recent configuration of the three considered and it is especially used for smaller communities and industrial installations with intermittent flows. It is a fill-and-draw type of reactor system involving a single completely-mixed reactor in which all steps of the activated sludge process occur. It gives more flexibility to the process and it can be operated as a selector process to minimize sludge bulking potential, due to the high F/M. On the other hand, the process control is more complicated and requires higher maintenance skills. Other types of configurations include the oxidation ditch, contact stabilization, Krause process, pure activated sludge, Orbal process and deep shaft aeration [23].

According to the Integrated Pollution Prevention and Control Report (European Commission, 2001) the typical removal efficiencies of a kraft pulp mill WWTP treated with the activated sludge process range from 85 - 98% for BOD₅ and 60 - 85% for COD. Phosphorus and nitrogen are reduced by 40 - 85% and 20 - 50% respectively. Generally, the treated effluent has the following concentration profile [14]:

Table 5 – Characterisation of the treated effluent from a Kraft pulp mill. Source: European Commission [14]

BOD₅ (mg O₂/L)	COD (mg O₂/L)	TSS (mg/L)	Total Phosphorus (mg P/L)	Total Nitrogen (mg N/L)
20 – 40	300 – 500	20 – 40	0.2 – 0.4	2 – 4

CHAPTER 3. WWTP MODELLING

3.1 INTRODUCTION

A model is a simplified representation of what occurs in the reality. It is defined by a series of mathematical equations and procedures, constituted by different variables and parameters dependent on time. A model allows studying and analysing engineering questions in a shorter period of time, reducing the costs associated with laboratory analysis. In a WWTP, models can be used to evaluate the system response to a variety of perturbations, thus allowing the implementation of strategies that guarantee a better performance. They are also useful for process optimization and control, for example to evaluate several scenarios that might lead to improved operation of existing WWTPs and design alternatives for new WWTP installations via simulation. In this context, modelling can substantially reduce the scale-up time, because different options can be evaluated before a pilot plant is built [24].

There are essentially two approaches when constructing an analytical model: mechanistic modelling and empirical modelling. Mechanistic models are based on an understanding of the behaviour of a system's components (white box approach) while empirical models are based on direct observation, cause-effect relations between the input and the output variables and extensive data records - regression modelling or neural networks (black-box approach). Empirical models are very simple but low on strength, since they are specific for a certain situation to which the relations were estimated. Mechanistic models, on the other hand, are more complex than empirical models because they try to describe all the processes that involve a certain phenomena based on a collection of differential equations, such as continuity equations, momentum and energy conservation, mass transport and biological reactions and thus they require a careful parameterization. While the empirical model is typically easier to construct, it provides less insight than the mechanistic model. The latter provides more realistic predictions and more can be done with it in terms of analyses, e.g., testing the sensitivities of the process to relevant parameters [25] [26].

3.2 MODELLING: STATE OF THE ART

In 1982, the IAWPRC – International Association on Water Pollution Research and Control, currently known as IAWQ – International Association Water Quality, established a Task Group in order to promote the development of studies on mathematical modelling towards the conception of a mechanistic model that could be used in a WWTP plant. The group focused on developing a simple mathematical model with realistic forecast capacity of the metabolic activity that happens in an activated sludge process, creating a solid work platform for future development of more complicated models. The final outcome was published in 1987 with ASM1 – Activated Sludge Model N°1. This model consists of stoichiometric and kinetic expressions that describe the biochemical transformations of soluble and particulate compounds in the activated sludge, namely the processes of carbonaceous oxidation, nitrification and denitrification. The components (COD, ammonia, oxygen) may be consumed or produced in these processes according to a set of yield coefficients. The rate of each biochemical process is expressed in a series of Monod-type kinetic reactions. The transformations described by ASM1 include aerobic growth of heterotrophs and autotrophs, anoxic growth of heterotrophs, decay processes for both heterotrophs and autotrophs and hydrolysis of soluble biodegradable COD and organic nitrogen compounds [27].

By the time that ASM1 was presented, some of the WWTPs had already included a line of treatment for the biological phosphorus (bio-P) removal. However, due to the lack of knowledge associated with this process, the IAWQ group decided not to include phosphorus modelling. During the following years, several phosphorus removal studies were conducted and thus, in 1995, appeared ASM2 – Activated Sludge Model N°2, which includes the biological phosphorus removal and also processes for phosphorus precipitation. Major additions to ASM2 include recognising a portion of heterotrophs as PAOs, which take up fermented carbon sources like volatile fatty acids (VFAs) and store them as PHA [28].

ASM2 did not include simultaneous phosphorus removal and denitrification by PAOs. This fact lead to the creation of an extended version, known as ASM2d, in 1999, which reflects the biological phosphorus removal achieved during denitrification as well as anoxic growth of PAOs. ASM2d became the most widely applied model incorporating EBPR – Enhanced Biological Phosphorus Removal [28].

In 1998, the group developed ASM3, a new modelling platform for the next generation of activated sludge models that was introduced to correct the deficiencies of ASM1. The ASM3 model assumes that all the readily biodegradable COD is first taken up and stored intracellularly, prior to biomass growth. The heterotrophic biomass is thus modelled with an internal cell structure, similar to PAOs in the bio-P removal models. A second difference

between ASM1 and ASM3 is that the latter model is easier to calibrate, due to the conversion of the circular growth-decay-growth model (ASM1), known as death-regeneration model, into a growth-endogenous respiration model (ASM3). This facilitates the calculation of endogenous decay rates that can be performed by respirometry [29].

The models of the ASM family are considered state-of-the-art models of activated sludge processes and are used in most of the modelling and simulation studies. However, other models and versions have emerged meanwhile such as the TUDP model, Mantis, Mantis 2 and others [30].

The TUDP model, developed by the Delft University of Technology, combines the metabolic model for denitrifying and non-denitrifying bio-P with the ASM1 model (autotrophic and heterotrophic reactions). Contrary to ASM2/ASM2d, this model considers the internal metabolism of phosphorus accumulating organisms and models all organic storage components explicitly [30].

The Mantis model, developed by the modelling software company Hydromantis, is a re-adaptation of ASM1, which includes the following modifications: two additional growth processes were introduced, one concerning the autotrophic organisms and one concerning the heterotrophic organisms, both occurring on low ammonia and high nitrate conditions; the kinetic parameters are considered temperature-dependent and aerobic denitrification was also introduced. Mantis 2 is the most recent model and includes a large amount of information that was published in the literature over the last decade, namely side stream treatment processes like struvite precipitation, nitrification-anammox for nitrogen removal and other precipitation processes [31].

There is also an increasing number of modelling studies concerning the microbial population dynamics. These include: denitrification with external methanol addition, with two groups of denitrifiers exhibiting different growth kinetics and yield coefficients with the purpose of selecting the most efficient denitrifier population [32]; competition between PAOs and GAOs (Glycogen accumulating organisms) and its metabolism using not only acetate but also propionate, incorporating production of other PHA fractions such poly-hydroxy-valerate (PHV) and poly- β -hydroxy-2-methylvalerate (PH2MV) [33] [34].

Also, an effort has been made in terms of modelling the activated sludge system with the other unit processes aiming to create an integrated control approach to the entire WWTP. An example is the Benchmark Simulation Model 1 (BSM1) that combines the ASM1 model with a detailed model of the settling dynamics in the second clarifier. Other extensions have been developed meanwhile in order to include primary clarifiers, sludge thickeners, sludge dewatering and anaerobic digestion processes [35] [36].

Furthermore, empirical models have been used in association with mechanistic models in line to create the concept of hybrid models – simplified mechanistic models that include data about process reactions, relying on a prediction of desired outputs (e.g. effluent ammonia, COD, phosphate). The empirical model serves as a “trained” artificial neural network which can adjust specific inputs (e.g. aeration intensity, recycle flow rates) to produce a specific target output. Hybrid models can be attractive options for process control purposes, especially due to the increasing accessibility of consistent on-line measurement tools [37].

All the models referred earlier are mainly applicable to municipal wastewater systems, but can be easily adapted to specific situations such as the presence of industrial wastewater. In particular, ASM models have been used on a variety of commercial softwares for biological process simulation, such as EFOR (Danish Hydraulic Institute), Simulink, BioWin (EnviroSim Associates Ltd. - Canada), SIMBA (SIMulation programs für die Biologische Abwasserreinigung), STOAT (Sewage Treatment Optimization and Analysis over Time - UK), WEST (Wastewater treatment plant Engines for Simulation and Training - Belgium) and GPS-X (Hydromantis Inc. – Canada) [38].

3.3 ASM2D - CHARACTERISATION

In this study the commercial software GPS-X 6.3 was used to simulate the activated sludge process that takes place in Portucel's WWTP. GPS-X is a modular, multipurpose modelling environment that uses an advanced graphical user interface to facilitate dynamic modelling and simulation. The simulator is built on the ACSL simulator that provides powerful integration and general simulator features. The biological models available in GPS-X are ASM1, ASM2d, ASM3, MANTIS and NEW GENERAL. The choice of the best model depends upon the processes that one is concerned about and the data/information available:

Table 6 – Processes covered by each model. Source: GPS-X Technical Reference [31]

Process:	ASM1	ASM2d	ASM3	MANTIS	NEW GENERAL
Fermentation Step		•			•
Nitrification/Denitrification	•	•	•	•	•
Aerobic denitrification				•	
Aerobic substrate storage			•		
COD "loss"					•
NO ₃ ⁻ as a N source for cell synthesis				•	•
Alkalinity consumption/generation	•	•	•	•	
Alkalinity (as a limiting factor for growth processes)		•			
Biological phosphorus removal		•			•
Precipitation of P with metal hydroxides		•			
Temperature dependency		•	•	•	•

Given that the biological processes that happens in Portucel's WWTP concern mainly the organic, nitrogen and phosphorus removal and since the pulp and paper mill release a considerable amount of metals such as Ca²⁺, the chemical precipitation of phosphorus was also an interesting process to take into account and thus the ASM2d model was the one chosen for modelling the WWTP.

COMPONENTS OF THE MODEL:

Model components are basically divided in state and composite variables. The first ones are known as the basic variables once that they are responsible for the system's characterisation (GPS-X's dynamic model of differential equations) and they are continuously integrated over time. On the other hand composite variables are obtained from the matrix product of state variables and stoichiometric constants. State and composite variables are the parameters that characterize a WWTP plant model and they give an overlook of how the WWTP is behaving at a certain moment. When GPS-X builds a model of a layout, it establishes a material balance for each state variable in the unit process and then calculates the corresponding composite variables [31].

Both of these variables can be characterized according to the two physical types of matter: soluble matter (S components) and particulate matter (X components). The soluble components are transported with the water during the treatment process and may carry ionic charge, whereas particulate components (electrically neutral) are associated with the activated sludge and therefore can be concentrated by sedimentation/thickening [28].

Soluble components:

- **S_I (soluble inert organic matter)** - biologically inert organics that are present in the influent matter but that can also be produced during the hydrolysis of particulate substrates. These components pass through the activated sludge system unchanged in form.
- **S_S (readily biodegradable organic substrate)** – these are simple molecules that may be taken in directly by heterotrophic bacteria and used for growth of new biomass, under aerobic or anoxic conditions. In the ASM2d model, the readily biodegradable organic substrate corresponds to the sum of fermentable readily biodegradable organic substrate (S_F) and the fermentation products (S_A ⁶). S_F represents the fraction of readily biodegradable substrate which serves as substrate for fermentation and S_A/S_{LF} represents the endproducts of fermentation, as explained further below. Readily biodegradable organic molecules are formed by hydrolysis of particulate organic matter.
- **S_{LF} (volatile fatty acids)** – low molecular mass carboxylic acids (C_2 - C_7 monocarboxylic aliphatic acids) like lactate, acetate, propionate and butyrate, formed during the anaerobic biodegradation of organic matter. In the biological treatment, they are consumed during aerobic growth of heterotrophs on fermentation products, storage of poly-hydroxy-alkanoates (PHA) by poly-P accumulating biomass and during

⁶ S_A – in GPS-X this parameter is called S_{LF} instead of S_A .

denitrification with fermentation products. They are formed during fermentation and lysis of PHA. For stoichiometric considerations they are considered to consist only of acetate.

- **S_O (dissolved oxygen)** – dissolved oxygen, normally in the form of air. Oxygen utilization is associated with heterotrophic/autotrophic growth and with aerobic storage and growth of poly-P by poly-P accumulating biomass.
- **S_P (soluble ortho-phosphate)** – inorganic soluble phosphorus. For the balance of electrical charges it is assumed to be 50% H_2PO_4^- and 50% HPO_4^{2-} . It is consumed during aerobic/anoxic storage and growth of poly-P by poly-P accumulating biomass and during precipitation of phosphates with metal hydroxides. It is formed during lysis of polyphosphates and redissolution of metal phosphates.
- **S_{NH} (free and ionized ammonia)** – ammonia nitrogen serves as nitrogen supply for synthesis of heterotrophic bacteria and as energy supply for growth of autotrophic nitrifying bacteria.
- **S_{NO} (nitrate and nitrite)** – Nitrate and nitrite are produced by aerobic growth of the autotrophic bacteria and are removed during anoxic growth of heterotrophic biomass (denitrification). For stoichiometric considerations they are assumed to completely be in the form of nitrate.
- **S_{NN} (dinitrogen)** – is the only nitrogenous product of denitrification. It may be subject to gas exchange, parallel with oxygen.
- **S_{ALK} (alkalinity)** – alkalinity of the wastewater. Alkalinity is introduced in order to obtain an early indication of possible low pH conditions. It is assumed to be bicarbonate only. All reactions that involve the addition or removal of species with a proton accepting capacity and/or removal of proton will cause changes in alkalinity. Examples of the latter are: conversion of ionized ammonia to amino acids during synthesis of heterotrophic and autotrophic biomass and the reversal of the process during ammonification; nitrification and denitrification.

Particulate components:

- **X_I (particulate inert organic matter)** – it is a fraction of the influent and it may also be produced in the context of biomass decay. It becomes trapped in the activated sludge and is removed from the system through sludge wastage.
- **X_S (slowly biodegradable substrate)** – this parameter is related to high molecular weight, colloidal and particulate organic substrates which must suffer cell external hydrolysis before they are available for degradation. In the process of hydrolysis they are converted into the readily biodegradable form and they are formed by decay of both heterotrophic and autotrophic biomass and also by lysis of poly-P accumulating biomass.
- **X_{BH} (active heterotrophic biomass)** – these organisms may grow aerobically and anoxically (denitrification) and be active anaerobically (fermentation). They are responsible for hydrolysis of particulate substrates and they are destroyed by decay.
- **X_{BA} (active autotrophic biomass)** – nitrifying organisms, responsible for nitrification. They are aerobic and chemo-litho-autotrophic.
- **X_{BP} (PAOs)** – these organisms are assumed to be representative for all types of polyphosphate-accumulating organism. X_{BP} does not include the cell internal storage polyphosphate and poly-hydroxy-alkanoates, but only the “true” biomass. The ASM2d model assumes that these organisms may grow in anoxic or aerobic conditions.
- **X_{BT} (poly-hydroxy-alkanoates (PHA))** – poly-hydroxy-alkanoates are cell internal storage products of polyphosphate-accumulating organisms (PAOs). For stoichiometric considerations PHA is assumed to have the chemical composition of poly-hydroxy-butyrate $(C_4H_6O_2)_n$. PHA are destroyed by lysis and during aerobic/anoxic storage and growth of PAOs.
- **X_{PP} (stored polyphosphate)** – polyphosphate is stored by PAOs under aerobic and anoxic conditions and is destroyed during lysis of PAOs and through storage of PHA by the PAOs.
- **X_{MeOH} (metal-hydroxides)** – responsible for the phosphorus-binding capacity. Metal-hydroxides may be present in the wastewater or may be added to the system. They are formed during the precipitation of phosphates with metal-hydroxides and destroyed during redissolution of metal phosphates.

- **X_{MeP} (metal-phosphates)** – this component results from binding phosphorus to the metal-hydroxides. They are formed during redissolution of metal phosphates and destroyed during the precipitation of phosphates with metal-hydroxides.
- **X_{TSS} (total suspended solids)** – this component is a lumped parameter consisting of all particulate components, both organic and inorganic. It is important to predict since is readily measurable in WWTPs.

KINETICS AND PROCESS RATE EQUATIONS

The kinetics and stoichiometry used to describe the processes are based on simple Monod kinetics for all components that can influence the reaction rates. According to AM2d model, there are five types of biological processes that take place in an activated sludge plant:

- Hydrolysis
- Processes concerning heterotrophic organisms (X_{BH})
- Processes concerning phosphorus accumulating organisms (X_{BP})
- Processes concerning nitrifying organisms (autotrophic organisms X_{BA})
- Simultaneous precipitation of phosphorus with ferric hydroxide ($Fe(OH)_3$)

The mathematical representation of rate equations can be found in the appendix (Appendix I – ASM2d rate equations), as well as the stoichiometric matrixes of the model. A summary of the description of state and composite variables for this model is shown in the next page.

Table 7 - State and composite variables defined in the ASM2d model – Part I. Source: GPS-X Technical Reference [31]

State Variables:	Designation:	Composite Variables:	Designation:
xii	Inert inorganic suspended solids (g/m ³)	x	Total suspended solids (g/m ³)
si	Soluble inert organic material (g COD/m ³)	vss	Volatile suspended solids (g/m ³)
ss	Readily biodegradable substrate (g COD/m ³)	xiss	Total inorganic suspended solids (g/m ³)
sf	Fermentable readily biodegradable substrate (g COD/m ³)	bod	Total carbonaceous BOD ₅ (g O ₂ /m ³)
slf	Volatile fatty acids (g COD/m ³)	cod	Total COD (g COD/m ³)
xi	Particulate inert organic material (g COD/m ³)	tkn	Total Kjeldahl nitrogen (g N/m ³)
xs	Slowly biodegradable substrate (g COD/m ³)	tp	Total phosphorus (g P/m ³)
xbh	Active heterotrophic biomass (g COD/m ³)	sbod	Filtered carbonaceous BOD ₅ (g O ₂ /m ³)
xba	Active autotrophic biomass (g COD/m ³)	xbod	Particulate carbonaceous BOD ₅ (g O ₂ /m ³)
xbp	Active poly-P accumulating biomass (g COD/m ³)	sbodu	Filtered ultimate carbonaceous BOD (g O ₂ /m ³)
xu *	Unbiodegradable particulates from cell decay (g COD/m ³)	xbodu	Particulate ultimate carbonaceous BOD (g O ₂ /m ³)
xsto *	Internal cell storage product (g COD/m ³)	bod	Ultimate carbonaceous BOD (g O ₂ /m ³)
xbt	Poly-hydroxy-alkanoates (PHA) (g COD/m ³)	scod	Filtered COD (g COD/m ³)
xgly *	Stored glycogen (g COD/m ³)	xcod	Particulate COD (g COD/m ³)
so	Dissolved oxygen (g O ₂ /m ³)	stkn	Filtered TKN (g N/m ³)
sp	Soluble ortho-phosphate (g P/m ³)	xtkn	Particulate TKN (g N/m ³)
xpp *	Stored polyphosphate (g P/m ³)	tn	Total nitrogen (g N/m ³)
xppr *	Stored polyphosphate (releasable) (g P/m ³)	stp	Filtered phosphorus (g P/m ³)
snh	Free and ionized ammonia (g N/m ³)	xtp	Particulate phosphorus (g P/m ³)

**Table 8 - State variables defined in the ASM2d model – Part II. Source: GPS-X
Technical Reference [31]**

State Variables	Designation:
snd *	Soluble biodegradable organic nitrogen (g N/m ³)
xnd *	Particulate biodegradable organic nitrogen (g N/m ³)
sno	Nitrate and nitrite (g N/m ³)
sni	Soluble unbiodegradable organic nitrogen (g N/m ³)
snn	Dinitrogen (g N/m ³)
salk	Alkalinity (mole/m ³)
xmeoh	Metal-hydroxides (g/m ³)
xmep	Metal-phosphates (g/m ³)

* Although these variables are defined in ASM2d, they are assumed to be equal to zero by the model.

Part II

Methods and Modelling

CHAPTER 4. METHODOLOGY

This chapter describes the methodology of modelling of Portucel's WWTP using GPS-X. Along the chapter, the following strategy was taken into account:

The first step was to portray the WWTP in terms of incoming effluents and physical data of the main unit operations. Secondly it was necessary to collect some historical data about the parameters that characterize the effluent during the entire treatment process in order to evaluate the efficiency of the plant and also to assemble data for the estimation of input parameters for the modelling.

The third step concerned the construction of the layout of the plant in GPS-X as well as the characterisation of input components, followed by the calibration of the model. The purpose of this last step was the fitting of the model in order to obtain a better approximation to the reality of the treatment process.

Lastly, a case study of the addition of urea was conducted: a series of simulations were done in order to analyse the effect of urea on the sludge production and treatment process efficiency. The simulation was validated in the WWTP at Portucel: the flow of urea was diminished to half the normal value and the results obtained were discussed.

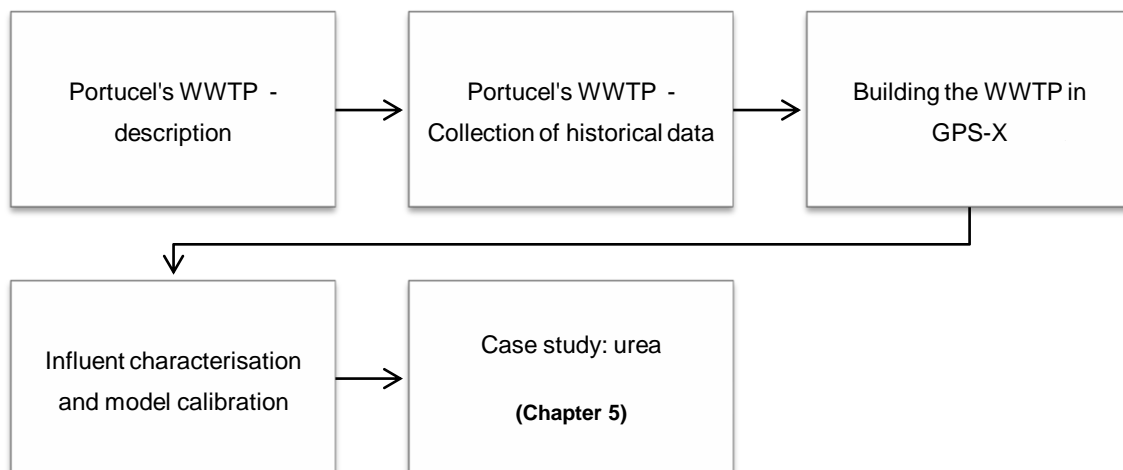


Figure 5 – Steps followed to simulate Portucel's WWTP.

4.1 PORTUCEL'S WWTP – description

The industrial complex of Portucel in Setúbal comprises two wastewater treatment plants: one that treats the wastewater resulting from the PPS⁷'s complex (the old paper mill) and the other one that is responsible for the treatment of wastewater coming from the pulp mill and ATF⁸ (the new paper mill). Both WWTPs are based on the activated sludge process, but the WWTP from PPS functions with an SBR, while the other functions with a plug-flow tank and it deals with a much larger quantity of wastewater. The latter was the WWTP chosen for this study.

The wastewater that comes from the pulp mill is classified as alkaline or acid. Alkaline wastewater corresponds to 56% of the total influent, has a pH of 7.0 to 10.0 and has high fiber content. Acid wastewater has a pH ranging from 3.0 to 4.0 and is originated from the bleaching section (D phases - Chlorine dioxide), SVP⁹, CHP¹⁰, demineralization and chemical products while the alkaline effluent comes from the remainder process sections. The effluent from ATF corresponds to 29% of the total influent and has a pH ranging from 7.0 to 10.0. The solid content is significantly variable and the content of starch is also considerable. The starch is added to paper in form of cationic starch in order to improve the resistance of the paper sheet, working as a retention agent.

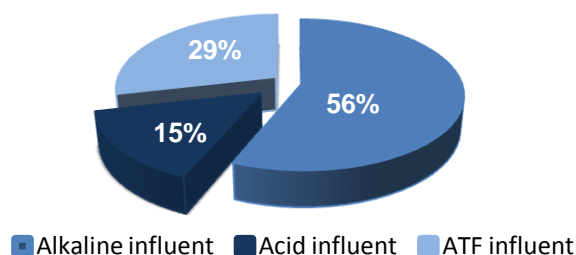


Figure 6 - Total influent distribution.

With regard to the treatment process, it can be divided in two stages: a primary treatment, designed to remove the majority of the fiber content of alkaline and ATF effluents; a secondary treatment, where the resulting treated effluent is gathered with the acid effluent to be treated by means of the activated sludge process. The primary treatment takes place in a rectangular clarifier and is preceded by a preliminary step of mechanical removal of solids and desanding.

The secondary treatment begins with the blending of the three influents in a subterranean chamber, called neutralization chamber. The mechanical mixing of these influents results in a mixed influent whose pH ranges from 6.0 to 9.0 and thus no neutralizing agent is needed. In the neutralization chamber nitrogen is added to the influent in the form of an aqueous solution of

⁷ PPS – Portucel Papel de Setúbal

⁸ ATF – About The Future

⁹ SVP – Chlorine dioxide generator

¹⁰ CHP – Combined Heat and Power

urea. This addition has the purpose of satisfying the nitrogen requirements for the biological treatment process. Since the temperature of the mixed influent ranges between 40 and 50°C it needs to be cooled in two cooling towers before entering in the aeration tank, to prevent a possible disturbance of the biological system's activity. The cooling step diminishes the influent's temperature to approximately 35 - 38°C. The influent is then discharged to the aeration tank that has an effective volume of 81,344 m³. The biological reactor has a plug-flow configuration and contains 28 submersible aerators (not uniformly distributed). The air feed to the aerators is given by two compressors with a maximum capacity of 20,000 Nm³/h each. The domestic influent is also discharged in the aeration tank but it comprises a very small quantity of the total influent housed by the tank. The hydraulic retention time in the aeration tank is about 40 to 50 hours. The tank has a middle wall and 6 "bridges" where the aerators are physically connected. The system functions with extended aeration. This allows microorganisms to keep growing and breaking down the sludge. As a result, less sludge is produced, limiting the volume of material produced by the system. The Solids Retention Time (SRT) of this system is about 19 - 20 days.

Next to the neutralization chamber and the aeration tank there is an emergency basin with a capacity of 30,000 m³. In the occurrence of an abnormal situation, for instance an unusually high temperature of the influent, extreme pH values or presence of toxic substances, the influent can be temporarily discharged to the emergency basin. This system works as a protection organ, providing stable conditions to the biological treatment process.



Figure 7 - View of part of the aeration tank at Portucel in Setúbal.

After the biological treatment the effluent is led to a chamber and is then distributed to both of the secondary clarifiers, in order to separate the liquid phase from the suspended solids. The clarifiers are circular and have a flat bottom configuration, a surface area of 2,642.04 m² and a water depth of approximately 4 meters.



Figure 8 - View of the secondary clarifiers at Portucel in Setúbal.

Subsequent to this unit process, the clarified effluent is connected to a Parshall flume, being discharged in the Sado river at 64 meters from the coast line. The majority of the sludge phase (95%) is recirculated to the aeration tank, in order to keep a TSS of 2,000 – 4,000 mg/L, while the remaining part is connected to a thickener to concentrate the TSS content of the sludge. The thickener also receives the sludge that comes from the PPS's WWTP.



Figure 9 - View of the thickener at Portucel in Setúbal.

The concentrated sludge (with an approximate consistency of 2%) is collected in a circular tank being later dehydrated in a filter press in order to obtain a consistency of 13 to 18%.



Figure 10 - View of the filter press at Portucel in Setúbal.

4.2 PORTUCEL'S WWTP – collection of historical data

Apart from the physical data of each process unit of Portucel's WWTP, laboratory information and daily operation bulletins were also consulted in order to collect information about the influent and effluent characteristics as well as some parameters concerning the aeration tank and secondary clarifiers.

With reference to the liquid effluents, analyses are made on the three types of influents (alkaline, acid and the effluent from ATF), samples from the cooling towers, aeration tank, secondary clarifiers and final effluent. The parameters analyzed cover the total suspended solids, COD and BOD₅, nutrients such as TKN (Total Kjeldahl Nitrogen) and TP (Total Phosphorus), colour, pH, AOX¹¹, sodium, bacteria and protozoa quantification, conductivity and fiber content. Regarding the sludge treatment, the parameters analyzed are organic and inorganic matter quantification, total suspended solids and consistency evaluation. The laboratory follows the standards of test, calibration and sample handling procedures described in the international standards ISO¹² and SMEWW¹³. All the data was consulted through the digital bulletins available on Portucel's database. These are daily laboratory reports that contain all the parameters measured by the laboratory's staff. The information concerning the dissolved oxygen (DO) and flow rates of specific unit processes was consulted in the daily operational bulletins that are filled by the WWTP operators [39].

The data collection for this study involved a daily temporal range of the last three years (2011, 2012 and 2013). The values shown on the tables refer to the overall average of the three years.

▪ Total Chemical Oxygen Demand (COD)

The method for COD measurement involved mixing the wastewater sample with two millimeters of a known mixture of potassium dichromate, sulfuric acid and mercury sulphate in closed reflux, at 148°C, for a period of two hours. This period is considered sufficient for part of the dichromate to be reduced by the oxidizable matter. The sample was then cooled to room temperature and the quantity of dichromate used in the oxidation was quantified through the absorbance measurement of chromium (III), by means of a photometer. Then, using a calibration curve, the COD of the sample was determined.

¹¹ AOX – Adsorbable Organically Bound Halogens, commonly known as Halogenated Organic Compounds

¹² ISO – International Organization for Standardization

¹³ SMEWW – Standard Methods for the Examination of Water and Wastewater

Table 9 - Average COD in the influent and effluent over the last 3 years.

	Average COD (g O₂/m³)	Target value for COD (g O₂/m³)
Influent (COD _{inf})	1,015 ± 169	< 1,500
Effluent (COD _{eff})	291 ± 45	< 570

In order to better evaluate the efficiency of the WWTP, the COD removal efficiency was calculated, using the following formula:

$$\text{COD}_{\text{removal efficiency}}(\%) = \frac{\text{COD}_{\text{inf}} - \text{COD}_{\text{eff}}}{\text{COD}_{\text{inf}}} \times 100 \quad (4.1)$$

The average efficiency of the three years was estimated as 71%, which is in accordance with the theoretical efficiency mentioned in Chapter 2 [14].

▪ **Biochemical Oxygen Demand (BOD₅)**

This test involved a five day incubation of the wastewater sample, at 20°C. Nutrients such as nitrogen, phosphorus and metals were added to the sample, which was then neutralized to insure an adequate pH value for the bacterial growth. A nitrification inhibitor was also added, usually sodium sulphate or chloro pyridine. The dissolved oxygen was measured initially and after incubation, using a specific sensor, called Oxitap. The BOD was obtained by the difference of the initial and final dissolved oxygen. This method is known as the respirometric method.

Table 10 - Average BOD₅ in the influent and effluent over the last 3 years.

	Average BOD₅ (g O₂/m³)	Target value for BOD₅ (g O₂/m³)
Influent (BOD _{5inf})	299 ± 52	< 400
Effluent (BOD _{5eff})	11 ± 3	< 40

With regard to the BOD₅ removal efficiency, it was calculated similarly to the COD removal efficiency and the average of 95% was obtained. Just like the average COD removal efficiency, the average BOD removal efficiency is also in accordance with the theoretical values [14].

In terms of the biodegradability of the influent, the average BOD₅/COD ratio for the last 3 years was equal to 0.3, which suggests that there is a considerable amount of non-biodegradable material in the influent.

▪ Total Kjeldahl Nitrogen (TKN)

The process of measuring total Kjeldahl nitrogen involved the digestion of the wastewater sample in the presence of sulphuric acid and a metal catalyst (copper), with the organic nitrogen being converted to ammonium sulphate (inorganic nitrogen). This digestion was carried out in two steps: the first step was conducted at 180°C during approximately 1.5 hour and the second was carried out at 380°C during half an hour. Then, the sample was distilled in the presence of sodium hydroxide with the nitrogen, in the gaseous form, being later re-collected and fixed in an acidified aqueous solution. Finally phenol and sodium nitroferricyanide dihydrate were added in order to develop colour and measure the TKN through spectrophotometry.

The laboratory measures the TKN only in the influent and final effluent. As it was mentioned earlier, urea is added to the influent, so it was necessary to take this nitrogen contribution into account. Experimental measures of the urea pump flowrate were taken during a full week and an average of 0.29 m³/day was obtained for the daily urea solution added by the pump. Since the content of nitrogen in the urea solution is 20.5% (w/w) and its specific gravity is 1,127 kg/m³, the daily flowrate of nitrogen obtained was 66.83 kg/day. Using the daily influent flowrates, available on Portucel's database, it was possible to calculate the final TKN concentration of the influent and effluent:

Table 11 - Average TKN in the influent and effluent over the last 3 years.

	Average TKN (g N/m³)	Target value for TKN (g N/m³)
Influent (TKN _{inf})	5.6 ± 0.7	-
Effluent (TKN _{eff})	1.9 ± 0.3	< 4.0
Average consumption of nitrogen		65.0%

The consumption of nitrogen for each month was calculated using the following formula:

$$\text{TKN}_{\text{consumption}} (\%) = \frac{\text{TKN}_{\text{inf}} - \text{TKN}_{\text{eff}}}{\text{TKN}_{\text{inf}}} \times 100 \quad (4.2)$$

▪ Total Phosphorus (TP)

The determination of total phosphorus involved a two step procedure: the first step consisted of a digestion of the wastewater sample with nitric and sulphuric acids, at 250°C. This digestion has the purpose of oxidizing the organic matter in order to free the phosphorus as orthophosphate. The second step consisted of determining the dissolved orthophosphate, by molecular absorption spectrophotometry, using the stannous chloride method. In this method, the sample was neutralized with sodium hydroxide and then, ammonium molybdate and stannous chloride were added to the sample, forming the molybdophosphoric acid which was then reduced by stannous chloride to form molybdenum blue.

Table 12 - Average of TP on the influent and effluent over the last 3 years.

	Average TP (g P/m³)	Target value for TP (g P/m³)
Influent (TP _{inf})	5.7 ± 1.3	-
Effluent (TP _{eff})	2.3 ± 0.6	< 4.0
Average consumption of phosphorus		55.0%

Regarding the BOD₅:N:P ratio, an approximate proportion of 100:1.83:1.77 was obtained, with an average BOD₅:N ratio of 54.75 and a BOD₅:P ratio of 56.39 (see Appendix III – BOD₅:N:P ratios), instead of the 100:5:1 expected from the literature [40]. This suggests that the amount of nitrogen that is being added to the influent is insufficient and also that the amount of influent phosphorus is greater than what is recommended. In relation to phosphorus there is nothing to be done, since the phosphorus present in the effluent is naturally high due to the nature of the wood. On the subject of nitrogen (urea) even though the quantity may seem insufficient, the WWTP has revealed a good performance and it does not seem to be lacking any nutrients.

▪ **Total Suspended Solids (TSS)**

In order to define the total suspended solids, it is necessary to define first the total solids (TS). The latter refers to the residue that remains after a wastewater sample has been evaporated and dried at 103 to 105°C. The total suspended solids is related to the portion of the total solids that are retained on a 1.58 µm pore size filter. Furthermore, the total suspended solids can be divided into volatile suspended solids (VSS) and fixed suspended solids (FSS). The VSS are the solids that can be volatilized and burned off when the TSS are ignited at 450 to 550°C, while the FSS correspond to the residue that remains after the ignition [16].

Table 13 - Average TSS in the influent and effluent, aeration tank and recirculated sludge streams, over the last 3 years.

	Average TSS (g/m³)	Target value for TSS (g/m³)
Influent (TP _{inf})	169 ± 44	< 150
Effluent (TP _{eff})	15 ± 4	< 40
Aeration tank	3,263 ± 353	2,000 – 4,000
Recirculated sludge	5,777 ± 669	4,000 – 6,000

The summary of main characterisation parameters of the Portucel's influent and effluent are shown in Table 14.

Table 14 - Summary of the main characterisation parameters for the influent and effluent of the WWTP.

Parameter:	Influent	Final effluent
Total COD (g O ₂ /m ³)	1,015 ± 169	291 ± 45
BOD ₅ (g O ₂ /m ³)	299 ± 52	11 ± 3
TKN (g N/m ³)	5.6 ± 0.7	1.9 ± 0.3
TP (g P/m ³)	5.7 ± 1.3	2.3 ± 0.6
TSS (g/m ³)	169 ± 44	15 ± 4

▪ **Other parameters**

- Dissolved oxygen profile in the aeration tank:

Table 15 - Average dissolved oxygen in the aeration tank over the last 3 years.

Section of the aeration tank	Average (g O₂/m³)	Target value (g O₂/m³)
(1)	0.50 ± 0.16	1.00 – 3.00
(2)	0.40 ± 0.16	
(3)	2.70 ± 0.63	
(4)	3.30 ± 0.65	
(5)	3.60 ± 0.79	
(6)	3.20 ± 0.95	
(7)	3.70 ± 0.98	
(8)	3.80 ± 0.94	

- SVI (Sludge Volume Index)

The sludge volume index was calculated using the values of clarified sludge (volume) and TSS (concentration) taken from a sample of recirculation sludge. The clarified sludge was obtained through the Imhoff's test: a sample of recirculation sludge was collected on an Imhoff vessel and after 30 minutes the volume of clarified/decanted sludge was registered.

$$SVI_{(i)} = \frac{\text{Volume of clarified sludge}_{(i)} (\text{mL} / \text{L})}{SST_{(i)} (\text{g} / \text{L})}, i = 1 \dots 36 (\text{month}) \quad (4.3)$$

Table 16 - Average of SVI over the last 3 years.

Average (mL/g)	Target value for SVI (mL/g)
159.65 ± 18.89	< 200.00

- Flow rates

Table 17 - Average flowrates over the last 3 years.

Flow rate	Overall average
Recirculation (each clarifier)	339.40 ± 61.60 (L/s)
Excess sludge (each clarifier)	14.38 ± 2.97 (L/s)
Sludge (output of the thickener)	14.40 ± 2.11 (L/s)
Sludge (output of the filter press) ¹⁴	152.90 ± 1.50 (m ³ /d)

¹⁴ This average was calculated based on two experimental weightings of the output sludge, considering a specific gravity of 904 kg/m³.

4.3 BUILDING THE WWTP IN GPS-X

- **Construction of the WWTP layout:**

As GPS-X builds dynamic process models based on a graphical representation of the unit processes, the first step was building Portucel's WWTP in a graphical form. In order to do that, objects (process unit icons) from the process table (GPS-X's unit process library) were chosen and connected through flow paths in order to build the WWTP process flow diagram, as it is shown below:

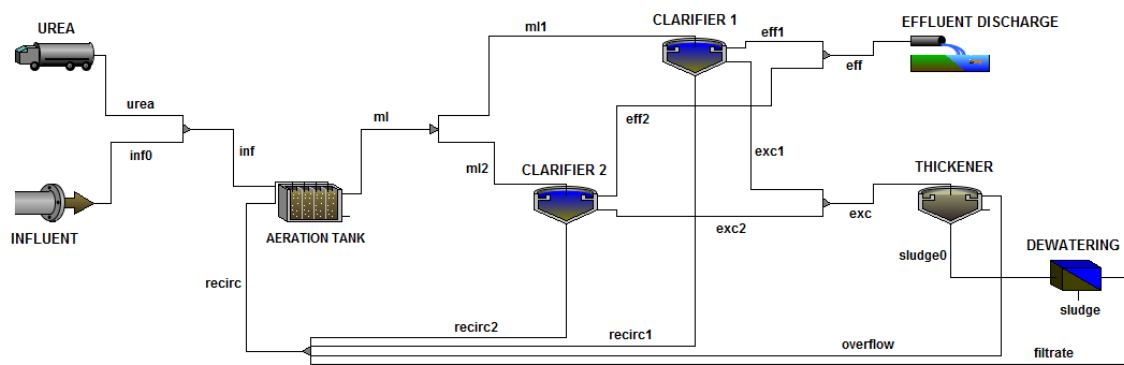


Figure 11 - Layout of Portucel's WWTP in GPS-X.

In terms of streams, inf0 refers to the influent (mixed influent) previously to the adding of urea, while inf refers to the stream of influent with the urea added. The stream ml/ml1/ml2 is related to the biologically treated effluent that exits the aeration tank. After the clarification step the effluent streams (eff1/eff2) are gathered to be discharged (eff), the excess sludge streams (exc/exc1/exc2) are pumped to the thickener and the recirculation streams from the clarifiers (recirc1/recirc2) are gathered with the thickener overflow and the filtrate from the filter press to originate the recirculation stream (recirc) that is pumped back to the aeration tank. The stream sludge0 refers to the concentrated sludge after the thickening and sludge refers to the concentrated sludge that exits the filter press (dewatering).

- **Selection of the library:**

Before proceeding to the physical characterisation of each unit process it was necessary to select the library that better suited the entire WWTP plant. A library is a collection of wastewater treatment components to which are inherent certain state variables. GPS-X has six libraries, each one of them having default values and expressions for the calculation of state variables. Since there was an interest in modelling carbon, nitrogen and phosphorus then, the Carbon, Nitrogen, Phosphorus (cnplib) library was chosen for this study. This library contains not only

carbon and nitrogen components but also phosphorus components that can be removed biologically or chemically. Overall, it contains 27 state variables [41].

- **Selection of the model for each process unit:**

For every process unit defined there is a set of models available to describe the behaviour of the object. The choice of the model depends basically on the information available to fill the user inputs necessary for the calculation of state and composite variables.

- **Influent:**

The characterisation of the influent wastewater is considered the basis of the simulated system as the characteristics of the influent affect the rest of the WWTP's behaviour. GPS-X offers six different models for the influent characterisation: bodbased, codfractions, codstates, sludge, states and tsscod. Since the data available from Portucel's database and laboratory concerned mainly the total COD, total TKN and total phosphorus, the model chosen for influent characterisation was the codstates. Using this model, most of the state variables whose value was not a user input value were calculated as a fraction of total COD. The software already has default values for these COD fractions; however, the user may change them in order to better calibrate the model of the WWTP plant.

- **Urea:**

To simulate the addition of urea a batch influent object was chosen, along with the codstates model, since the main parameters used to describe this operation were the urea's COD and its nitrogen content.

- **Aeration Tank:**

As it was referred in CHAPTER 3, ASM2d was the model selected to describe the biological treatment in the aeration tank.

- **Clarifiers:**

For the modelling of the clarification GPS-X offers three types of models:

- Zero-dimensional, nonreactive: point;
- One-dimensional, nonreactive: simple1d;
- One-dimensional, reactive: mantis, asm1, asm2d, asm3, newgeneral.

In reactive models, biological reactions are included and the models are associated with the corresponding suspended-growth models described in Chapter 3. Since it was observed that the COD level at the end of the aeration tank agreed well with the COD in the final effluent, biological reactions were considered to happen in a small extension in the clarifiers and

therefore the model simple 1d was the one chosen for this study. This is a first-order model, proposed by Takács et al. (1991) and assumes that the incoming solids are distributed instantaneously and uniformly across the entire cross-sectional area of the feed layer and only vertical flow is considered (there is no dispersion). It divides the clarifier into 10 layers of equal thickness as it is shown below [42] [43]:

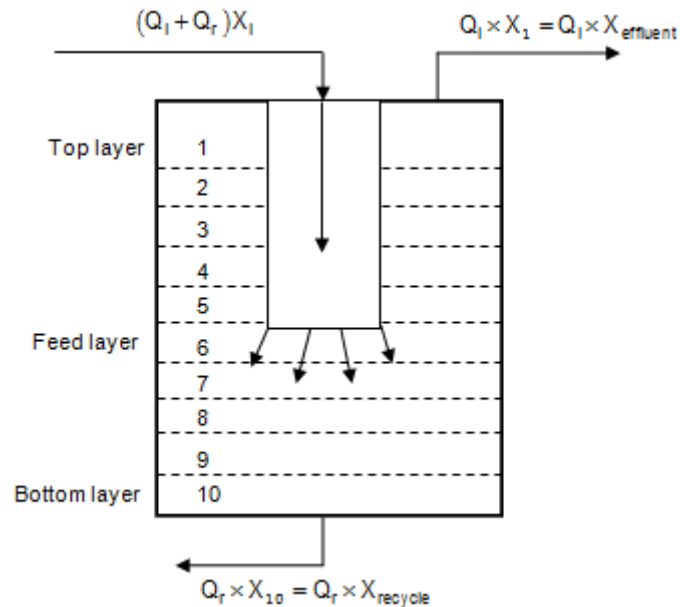


Figure 12 - Simple1d model - scheme of the 10 - layer clarification. Source: GPS-X Technical Reference [31].

The model is based on the solids flux concept: a mass balance is performed around each layer. There are five different groups of layers, depending on their position relative to the feed point. The solids flux in a particular layer is limited by what can be handled by the adjacent layer. The solids flux due to bulk movement of the liquid is a straightforward calculation based on the solids concentration and liquid bulk velocity, which is up or down depending on its position relative to the feed layer.

In the simple1d model, the only numerically integrated variable is the suspended solids concentration. The concentrations of particulate state variables in the influent to the clarifier (heterotrophic organisms, etc.) are stored as fractions of the total suspended solids concentration entering the clarifier. The concentrations of soluble state variables are not changed in this model.

- **Thickener and Dewatering:**

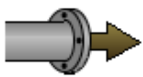


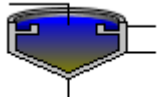


To describe these operations the following models were available [31].

- Thickener: empiric and simple1d;
- Dewatering – asce, differential, empiric, highrate, press and simple.

Due to the lack of specific data such as the solids capture, minimal sludge concentration for processing and organic and nutrient fractions of the sludge, the model chosen for modelling these unit processes was the empiric model. This model demands the specification of the underflow/pumped flow rate and concentration removal efficiency. Once these parameters are added, the model performs a mass and flow balance to determine the flow and concentrations for the cake (sludge) and filtrate/overflow streams.

▪ **Physical and operational data:**

Table 18 - Physical and operational data.

Process Unit	Physical Parameter	Value	Operation Parameter	Value
 Wastewater Influent	-	-	Flow Data	41,874.97 m ³ /d (daily average of August 2013)
 Urea influent	-	-	Flow Data	Daily average – 0.29 m ³ /d
 Aeration Tank	Number of reactors (fractions)	8	Aeration Method	Diffused air
	Tank depth	10 m	Total airflow	31,970.84 m ³ /h
	Maximum volume	81,344 m ³	Influent fractions	ml(1) – 1
	Liquid temperature	35°C	Recycle fractions	ml(1) – 0.7 ml(2) – 0.3
	Blower inlet temperature	60°C	-	-
	Elevation above sea level	17 m	-	-
 Clarifier	Clarifier type	Flat Bottom	Underflow rate	339.4 L/s
	Surface	2,642.08 m ²	Pumped flow	14.38 L/s
	Water depth	4 m	Sludge blanket threshold concentration	6,000 mg/L
	-	-	Design MLSS concentration	3,000 mg/L
 Thickener	Surface area	314.16 m ²	Pumped flow	14.4 L/s
	Depth	4 m	Removal efficiency (concentration basis)	0.985
 Dewatering	-	-	Pumped flow	152.9 m ³ /d
	-	-	Removal efficiency (concentration basis)	0.95

4.4 INFLUENT CHARACTERISATION AND MODEL CALIBRATION

Once the input of physical data was completed, the wastewater and urea influents were characterized, namely in terms of COD composition and COD fractions.

Urea influent:

Since the addition of urea was basically an addition of nitrogen and COD, the main input parameters were the total COD and TKN. Therefore, the COD of a sample of a urea solution sample was measured in Portucel's laboratory, and the value of 117 g COD/m³ was obtained. Regarding the TKN, the amount of nitrogen present was considered to be uniquely free and ionized ammonia and it was quantified as 231,035 g NH₄⁺/m³. This value was obtained through the specific gravity of the urea solution (1,127 kg/m³) and the nitrogen composition of the solution (20.5% (w/w)).

The rest of the input parameters were set as zero with the exception of an influent and an organic fraction. The influent fractions are composed of the following ratios:

Table 19 – Input of influent fractions (urea influent).

Symbol:	Description:	GPS-X default values
icv	XCOD/VSS ratio	<u>1.8</u>
fbod	BOD ₅ /BOD ultimate ratio	0.66
ivt	VSS/TSS ratio	0.75

XCOD stands for the particulate COD and BOD ultimate is related to the total amount of oxygen consumed when the biochemical reaction is allowed to proceed to completion. Since the TSS in the solution of urea is practically zero, and as the TSS is not an input parameter but a composite variable, the first ratio (XCOD/VSS) was iteratively manipulated with the intention of obtaining a minimum quantity of solids in the characterisation. Thus, a final ratio of XCOD/VSS resulted in 12.0 with 1.95 g/m³ of total suspended solids.

In relation to the organic fractions (see Table 20), the fractions frsf, frslf, frxbh, frxba, frxbp and frxbt were set as zero because there is no presence of microorganisms or substrate in the urea solution. The particulate inert fraction of total COD (frxi) was set as the default value and the soluble inert fraction of total COD (frsi) was estimated as 0.85, in order to obtain the 1.95 g/m³ of total suspended solids described above.

Table 20 – Input of organic fractions (urea influent).

Symbol:	Description:	GPS-X default values
frsi	Soluble inert fraction of total COD	<u>0.05</u>
frsf	Fermentable biodegradable fraction of total COD	<u>0.2</u>
frslf	VFA fraction of total COD	0
frxi	Particulate inert fraction of total COD	0.13
frxbh	Heterotrophic biomass fraction of total COD	0
frxba	Autotrophic biomass fraction of total COD	0
frxbp	PolyP biomass fraction of total COD	0
frxbt	PHA fraction of total COD	0

Wastewater influent (mixed influent):

The characterisation of the mixed influent was the most important step of the modelling and it involved a careful analysis. The majority of the parameters were calculated based on the historical data mentioned before (see Table 14). According to Roeleveld et al.: “Originally the simulation studies started with a long (1 - 4 weeks) intensive measurement campaign collecting and analyzing hundreds of samples, and even potentially checking many of the model parameters by respirometry or other tests. This is an expensive and long lasting procedure. It can be shown that many parameters in full-scale systems are hardly sensitive and therefore experimental evaluation of these parameters is not useful.” Therefore the development of the model should rely as much as possible on historical data in order to save time and costs and make the use of modelling more feasible [44].

The total COD was initially set as the overall average (1,015 g COD/m³) and the same for the TKN (4.0 g N/m³) and total phosphorus (5.7 g P/m³). Similarly to the urea influent, the TKN was considered to be uniquely free and ionized ammonia and the total phosphorus was considered to be 100% ortho-phosphate:

Table 21 – Phosphorus and nitrogen fractions (wastewater influent).

Symbol:	Description:	Considered values:
frxsp	Ortho-phosphate fraction of soluble phosphorus	1
frxpp	xpp fraction of particulate phosphorus	0
frsnh	Ammonium fraction of soluble TKN	1
frsni	Inert fraction of soluble TKN	0

The alkalinity was set as the default value of 7 mole $\text{HCO}_3^-/\text{m}^3$. For the calculation of the metal-hydroxides fraction, a sample of the influent wastewater was analysed via atomic absorption spectrometry. The values of 66.39 g/m^3 and 14.29 g/m^3 were obtained for the concentrations of calcium and magnesium in the influent, respectively. Although it was just one experimental measurement, these were the concentrations considered for the modelling. The total metal-hydroxide concentration in the influent was then estimated in 80.68 g/m^3 . This metal concentration is related to an addition in the chemical oxygen demand, since the metals are considered as inert material. Therefore, the total COD value of 1,015 $\text{g COD}/\text{m}^3$ was corrected to 1,095.68 $\text{g COD}/\text{m}^3$.

Since the metal-hydroxide fraction, frxmeoh , is defined as a fraction of the inorganic suspended solids, it was necessary to define first this parameter, more specifically, the total suspended solids. As it was mentioned before, the TSS is a composite variable that depends on the XCOD/TSS ratio. This ratio was iteratively manipulated with the purpose of obtaining a TSS of 169 g/m^3 (overall average – historical data) + 80.68 g/m^3 (metal-hydroxides) = 249.68 g/m^3 . For the VSS/TSS ratio prediction, analyses were conducted in Portucel's laboratory during a full week, and the average value obtained for this ratio was 0.51 (considering the metal precipitates).

Regarding the $\text{BOD}_5/\text{BOD}_{\text{ultimate}}$ ratio, an attempt of calculating the BOD ultimate was first taken, using the expressions determined by Roeleveld and van Loosdrecht [45]:

$$\text{BOD}_{\text{ultimate}} = \frac{1}{1 - e^{-k_{\text{BOD}} \times t}} \times \text{BOD}_t \quad (4.4)$$

Where k_{BOD} is the organic material degradation constant (d^{-1}), t refers to the days of incubation (5 days in this study) and BOD_t refers to the BOD_5 . Using the value of 0.32 d^{-1} , obtained by the authors through fitting methods, the value of 374 $\text{mg O}_2/\text{L}$ was achieved for the overall average of the three years at analysis. Using the historical average value of 299 $\text{mg O}_2/\text{L}$ for BOD_5 , the $\text{BOD}_5/\text{BOD}_{\text{ultimate}}$ ratio would result in 0.8. However the input of this value in the influent characterisation did not lead to the desired BOD_5 value of 299 $\text{g O}_2/\text{m}^3$. A possible explanation could be that the value of 0.32 d^{-1} , estimated for municipal wastewaters, may not be applicable in this study. As a consequence, the $\text{BOD}_5/\text{BOD}_{\text{ultimate}}$ ratio was iteratively manipulated in order to obtain a BOD_5 near 299 $\text{g O}_2/\text{m}^3$. The resulting ratios and metal fractions are shown:

Table 22 - Input of influent fractions (wastewater influent).

Symbol:	Description:	Considered values:
icv	XCOD/VSS ratio	1.46
fbod	BOD ₅ /BOD ultimate ratio	0.43
ivt	VSS/TSS ratio	0.51

Table 23 – Input of metal precipitates fractions (wastewater influent).

Symbol:	Description:	Considered values:
frxmeoh	metal-hydroxide fraction of inorganic suspended solids	0.65
frxmep	metal-phosphate fraction of inorganic suspended solids	0

Once again, the metal-hydroxide fraction was iteratively manipulated with the purpose of obtaining a xmeoh close to 81 g/m³. The metal-phosphate fraction was set as zero because the particulate phosphate concentration in the influent can be considered negligible. In relation to the nutrient fractions, these were initially set as the default values of GPS-X:

Table 24 - Nutrient fractions (wastewater influent).

Symbol:	Description:	GPS-X default values:
insi	N content of soluble inert material	0.01
insf	N content of fermentable substrate	0.03
inbm	N content of active biomass	0.07
inxi	N content of particulate inert material	0.02
inxs	N content of particulate substrate	0.04
ipsf	P content of fermentable substrate	0.01
ipsi	P content of soluble inert material	0.00
ipxi	P content of particulate inert material	0.01
ipxs	P content of particulate substrate	0.01
ipbm	P content of active biomass	0.02

Regarding the organic fractions, the presented guidelines were followed, based on Roeleveld and van Loosdrecht [45]:

1. Determination of S_I based on the inert soluble COD in the influent of the WWTP;
2. Determination of S_S by subtracting the fraction S_I from the soluble COD in the influent;

$$\text{COD}_{\text{soluble}} = S_S + S_I \Leftrightarrow S_S = \text{COD}_{\text{soluble}} - S_I \quad (4.5)$$

3. Determination of X_S by subtracting the fraction S_S from the biodegradable COD (bCOD);

$$\text{bCOD} = S_S + X_S \Leftrightarrow X_S = \text{bCOD} - S_S \quad (4.6)$$

4. Determination of X_I .

$$\begin{aligned} \text{COD} &= \text{COD}_{\text{soluble}} + \text{COD}_{\text{particulate}} \\ \Leftrightarrow \text{COD} &= S_I + S_S + X_I + X_S \\ \Leftrightarrow X_I &= \text{COD} - S_I - S_S - X_S \end{aligned} \quad (4.7)$$

The soluble inert organic material was estimated using the expression proposed by Roeleveld and van Loosdrecht [45]:

$$S_I = 0,9 \times \text{COD}_{\text{effluent,soluble}} \quad (4.8)$$

The soluble COD of the influent and effluent was measured four times in Portucel's laboratory. For each measurement the corresponding soluble COD/total COD ratio was calculated and using the average ratio, the total COD data from the last three years was converted to soluble COD values.

The biodegradable COD (bCOD) was obtained using, once again, using an expression suggested by Roeleveld and van Loosdrecht [45]:

$$\text{bCOD} = \frac{1}{1 - f_{\text{BOD}}} \times \text{BOD}_{\text{ultimate}} \quad (4.9)$$

Where f_{BOD} ($=0,15$) is a correction factor.

According to this calculation procedure, for the majority of the 36 months considered (12 months x 3 years), the X_S variable resulted in a negative value, which is physically impossible. This problem is likely due to either a wrong estimation of $\text{BOD}_{\text{ultimate}}$ and bCOD, or alternatively, an inappropriate extrapolation of the soluble COD/total COD ratio. Therefore, it was proved that a certain calibration of these organic parameters would be useful.

As stated by the STOWA¹⁵ protocol for dynamic modelling of activated sludge systems, the best way to calibrate the model is through a stepwise procedure: (i) sludge composition, (ii) nitrification and denitrification, (iii) internal flows [44].

(i) Sludge composition

The sludge composition is mainly affected by the influent characterisation, namely in terms of the organic fractions. Attending to the following expression:

$$1.0 = \text{frsf} + \text{frslf} + \text{frsi} + \text{frxi} + \text{frxs} + \text{frxbh} + \text{frxba} + \text{frxbp} + \text{frxbt} \quad (4.10)$$

Since the biomass and PHA fractions are typically set as zero in the influent characterisation, the fractions that required calibration were: frsf, frslf, frsi, frxi and frxs.

▪ FRSI

Since there was no way of predicting experimentally the soluble inert organic material, the expression (equation 4.8) proposed by. Roozeveld and van Loosdrecht [45] was assumed as valid and so the frsi fraction was calculated by:

$$\text{frsi} = \frac{\overline{S_i}}{\text{COD}} = \frac{251.85}{1,095.68} = 0.23 \quad (4.11)$$

▪ FRSLF

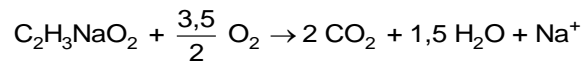
The volatile fatty acids (S_{LF}) were determined by high-performance liquid chromatography (HPLC). S_{LF} was considered to be equal to the chemical oxygen demand of the volatile fatty acids detected. Since all the volatile fatty acids are considered to be acetate by the model, the total VFA's were converted to acetate as follows:

Table 25 - Results of the VFA's quantification in an influent sample, using the method of HPLC.

Components:	Concentration of the peak (g/m ³):
Acetate	81.80
Propionate	104.05
Lactate	50.16
Total VFA's (g VFA/m³)	236.01

¹⁵ STOWA- Dutch Foundation of Applied Water Research

Considering the chemical oxidation of the acetate:



The COD of the volatile fatty acids resulted in:

$$\text{COD}_{\text{VFA}} = 236.01 \text{ g acetate} / \text{m}^3 \times \frac{3,5}{2} \times \frac{32 \text{ g O}_2 / \text{mole}}{59 \text{ g acetate} / \text{mole}} = 252.01 \text{ g O}_2 / \text{m}^3 \quad (4.12)$$

And thus:

$$\text{frsi} = \frac{\text{COD}_{\text{VFA}}}{\text{COD}} = \frac{252.01}{1095.68} = 0.23 \quad (4.13)$$

▪ FRSF, FRXI and FRXS

A first attempt of determining these organic fractions consisted in using the values of the influent soluble and particulate COD, attending to the fact that:

$$\frac{\overline{\text{COD}}_{\text{soluble}}}{\overline{\text{COD}}} = \text{frsi} + \text{frsf} + \text{frslf} \quad (4.14)$$

And:

$$\frac{\overline{\text{COD}}_{\text{particulate}}}{\overline{\text{COD}}} = \text{frxi} + \text{frxs} \quad (4.15)$$

As the ratio soluble COD/COD has the value of 0.82, the frsf resulted in 0.36. Assuming that there is no slowly biodegradable substrate in the influent, frxs = 0, and as the ratio of particulate COD/COD has the value of 0.18 so, frxi = 0.18. However, the simulation results using these values for the input of organic fractions did not lead to the desirable output concentrations:

Table 26- Target values for the main output streams.

Output parameter:	Target values (Portucel's historical data):
TSS of ml (exit stream of the aeration tank)	3,263 g/m ³
TSS of recirculation and excess sludge streams	5,777 g/m ³
TSS of sludge (final sludge stream after dewatering)	18,231 kg/d
TSS of the final effluent	15.3 g/m ³
COD of the final effluent	291 g O ₂ /m ³

Table 27 - Output concentrations after simulation.

Organic Fractions:	Output parameter:	Value after simulation:
frsf = 0.36	TSS of ml (exit stream of the aeration tank)	3,490 g/m ³
frslf = 0.23	TSS of recirculation and excess sludge streams	6,266 g/m ³
frsi = 0.23	TSS of sludge (final sludge stream after dewatering)	14,770 kg/d
frxi = 0.18	TSS of the final effluent	14.5 g/m ³
frxs = 0	COD of the final effluent	266 g O ₂ /m ³

The problem may lie on the following facts: the estimated average soluble COD/total COD ratio (0.82) may not be suitable for all the COD historical data extrapolation, and/or the slowly biodegradable substrate concentration is higher than expected – there might be colloidal and particulate organic substrates in the influent, which must suffer cell external hydrolysis before they are available for degradation. Upon this, a sensitivity analysis was done, through changing the values of frsf, frxi and frxs and consequently the values of the soluble and particulate COD ratios. This analysis had the purpose of evaluating the effect of the range of organic fractions on the output concentrations of the exit streams. A qualitative summary of this analysis is shown below:

Table 28 - Results of the sensitivity analysis done to frxi, frsf and frxs.

Organic Fractions:	Effect on the main output streams:
↑ frxi; ↓ frsf ; = frxs (0)	↑ TSS of ml (exit stream of the aeration tank)
	↑ TSS of recirculation and excess sludge streams
	↑ TSS of sludge (final sludge stream after dewatering)
	= TSS of the final effluent
	↓ COD of the final effluent (not very significant)
↓ frxi; ↑ frsf ; ↑ frxs	↓ TSS of ml (exit stream of the aeration tank)
	↓ TSS of recirculation and excess sludge streams
	↓ TSS of sludge (final sludge stream after dewatering)
	↓ TSS of the final effluent (not very significant)
	↑ COD of the final effluent (not very significant)

As can be seen, bigger values of fr_{xi} translate into higher sludge production, namely in the recirculation and excess streams, which is not desirable for the fitting of the model. The TSS of the final effluent depends mainly on fr_{si} and as this fraction was not changed during the course of the sensitivity analysis (since it already described well the data of Portucel) the TSS of the final effluent remained the same. In relation to the effluent's COD, it depends on fr_{sf} and fr_{slf} . The latter was maintained the same (since it was determined experimentally), similarly to fr_{si} , and no significant change was observed when fr_{sf} was ranged. High values of fr_{xs} were desirable for the fitting of the model since they translated into a smaller fr_{xi} value, and consequently, into a smaller recirculation and excess sludge production.

On the other hand, a sensitivity analysis concerning the stoichiometric and kinetic parameters was also done. Considering the values listed in Table 27 for the influent organic fractions, the heterotrophic biomass yield (Y_H) was sequentially changed from its default value (0.625 g COD/g COD) to lower values (minimum 0.3 g COD/g COD) and the results obtained in terms of TSS and COD of the main streams were analyzed. A similar procedure was taken regarding the rate constant for lysis and decay (b_H): its default value (0.4 d^{-1}) was sequentially increased until a value close to 0.7 d^{-1} . It was expected that either of these parameters modifications would translate into a lower TSS content in the sludge, since the decrease of biomass yield and/or increase of cell decay would result in a slower biomass concentration and consequently, in a slower TSS in the sludge. However, the simulation results showed that neither of these two modifications decreased significantly the TSS content of the sludge. Thus, these parameters were maintained at their original default values.

As a result, the strategy taken to estimate the fr_{sf} , fr_{xi} and fr_{xs} was through increasing the influent's soluble COD/COD ratio as little as possible in order to obtain output concentrations that fit the result of the output concentrations measured at Portucel. Finally, a soluble COD/COD ratio of 0.83 was found (instead of 0.82), and the X_i was considered to be 76% of the influent's particulate COD, leaving 24% for the slowly biodegradable substrate, X_S . As a consequence, fr_{sf} assumed the value of 0.37 (instead of 0.36):

Table 29 - Summary of the estimated organic fractions for the influent characterisation.

fr_{sf}	fr_{slf}	fr_{si}	fr_{xi}	fr_{xs}
0.37	0.23	0.23	0.13	0.04

The high presence of particulate inert material is likely due to the fact that soluble colloidal material (lignin, for instance) can be adsorbed to the biomass, and since it is not biodegraded, it remains as particulate inert material.

Regarding the concentrations of the main output streams, the following results were obtained as the best fitting achieved:

Table 30 - Comparison of the concentrations of the main output streams given by the historical data from Portucel and by the simulation using GPS-X.

Output parameter:	Target Value (Portucel's historical data):	Results from the simulation:
TSS of ml (exit stream of the aeration tank)	3,263 g/m ³	3,262 g/m ³
TSS of recirculation and excess sludge streams	5,777 g/m ³	5,479 g/m ³
TSS of sludge (final sludge stream after dewatering)	18,231 kg/d	12,920 kg/d
TSS of the final effluent	15.3 g/m ³	12.5 g/m ³
COD of the final effluent	291 g O ₂ /m ³	263 g O ₂ /m ³

Comparing the obtained fractions with values from other studies (see Table 31), it can be seen that the fraction frss, which results from the sum of frsf and frslf, has a higher value than the one predicted by other authors. This is probably due to the significant value of volatile fatty acids contained in this influent (frslf=0.23). Furthermore, the particulate material fractions, frxs and frxi are also different from the ones of the studies. Barañao and Hall have predicted a higher value for the slowly biodegradable substrate fraction and a lower value for the particulate inert fraction. The influent of Portucel is also a Bleached Kraft Mill Effluent (BKME). The study made by Stanyer differs significantly from the obtained results of this work, while the study made by Slade shows a similar result in terms of particulate inert.

Table 31 - Summary of COD influent fractions from similar studies. Source: P. Barañao and E. Hall [46]

COD fraction	P. Barañao and E. Hall [46]	Stanyer [47]	Slade [48]	Sreckovic [49]
S _s	0.49	0.24 – 0.44	0.42	0.28
S _i	0.14	0.32 – 0.36	0.33	0.33
X _s	0.30	0.23 – 0.42	0.11	0.11
X _i	0.07	0.03 – 0.07	0.14	0.05
Mill type	CTMP ¹⁶	BKME ¹⁷	BKME	CTMP

¹⁶ CTMP - Chemi-thermomechanical pulp

¹⁷ BKME – Bleached Kraft Mill Effluent

(ii) Nitrification and denitrification

According to Roeleveld and van Loosdrecht, the nitrogen fractions for the various COD components can be found by fitting the model on the measured nitrogen content of the sludge. [45]. During the year of 2014, Portucel requested two analyses for nitrogen and phosphorus measurement in the dehydrated sludge. The results of these analyses are shown on the table below:

Table 32 - Results from the analysis of N and P content in the dehydrated sludge.

Date:	N content of the sludge	P content of the sludge
08 – 01 – 2014	2.10×10^4 mg/kg (2.10%)	4.20×10^3 mg/kg (0.42%)
14 – 03 - 2014	9.90×10^3 mg/kg (0.99%)	2.60×10^3 mg/kg (0.26%)

As shown, the maximum content of nitrogen in the dehydrated sludge was measured as 2.10% while for the phosphorus, the content is significantly lower (0.42%). Table 33 shows the results related to the N and P content of the main output streams, obtained by the previous simulation:

Table 33 - Results of the N and P content of the main output streams obtained by the simulation.

Output parameter:	Results from the simulation:
N content of the dehydrated sludge	2.32 %
P content of the dehydrated sludge	3.50 %
TKN in the final effluent	3.21 g N/m^3
Total nitrogen in the final effluent	6.98 g N/m^3
Total phosphorus in the final effluent	0.65 g P/m^3

Keeping in mind that the average concentration of TKN and total phosphorus in Portucel's effluent is, respectively, $1.9 \pm 0.3 \text{ g N/m}^3$ and $2.3 \pm 0.6 \text{ g P/m}^3$ the subsequent conclusions were withdrawn: the N and P content of the dehydrated sludge was excessive compared with the target values of Portucel, particularly in the case of phosphorus precipitation and the TKN and total nitrogen contents in the final effluent were also excessive compared with the target values.

In particular, the software was predicting the occurrence of an excessive nitrification, due to the high concentration of nitrates and nitrites (obtained by subtracting the total nitrogen to the TKN). However, in the WWTP of Portucel the concentration of nitrates and nitrites in the effluent is minimal, which suggests a very low level of nitrification performed by the sludge. Finally, the total phosphorus obtained by the simulation was below the average, which could indicate that a lot of phosphorus was being precipitated instead of passing through the effluent.

In order to fit the model to a better nitrogen and phosphorus removal, the following strategy was adopted:

- the initial concentration of autotrophs in the aeration tank was set as zero, in order to minimize the possibility of nitrification;
- the influent nutrient fractions, set initially as the default values, were changed: the N content of the particulate inert material, *inxi*, particulate substrate, *inxs*, soluble inert material, *insi* and fermentable substrate, *insf*, were set as zero with the purpose of minimizing the N content in the sludge and in the final effluent. For what concerns the phosphorus, the particulate fractions were also set as zero in order to minimize the P content in the sludge and the P content of the soluble inert material, *ipsi*, was changed from 0 to 0.007 in order to obtain a higher phosphorus concentration in the final effluent.

Table 34 – Modifications in the N and P fractions.

Symbol:	Description:	GPS-X default value:	Considered value:
<i>inbm</i>	N content of active biomass	0.07	0.07
<i>inxi</i>	N content of particulate inert material	0.02	0
<i>inxs</i>	N content of particulate substrate	0.04	0
<i>insi</i>	N content of soluble inert material	0.01	0
<i>insf</i>	N content of fermentable substrate	0.03	0
<i>ipbm</i>	P content of active biomass	0.02	0.02
<i>ipxi</i>	P content of particulate inert material	0.01	0
<i>ipxs</i>	P content of particulate substrate	0.01	0
<i>ipsi</i>	P content of soluble inert material	0	0.007
<i>ipsf</i>	P content of fermentable substrate	0.01	0

As a result the output concentrations of the new simulation fitted Portucel's results in a very good way and thus the calibration of the model was considered complete. These modifications did not change the COD and TSS values of the final effluent, as predicted. The calibration of the internal flows (iii step) was not considered to be necessary, since the model was already calibrated and also based on the fact that the pump flow rates were experimentally verified prior to model calibration.

Table 35 - N and P concentrations in the dehydrated sludge and final effluent after the modifications.

Output parameter:	Results from the simulation:
N content of the dehydrated sludge	1.14 %
P content of the dehydrated sludge	1.75 %
TKN in the final effluent	2.20 g N/m ³
Total nitrogen in the final effluent	2.20 g N/m ³
Total phosphorus in the final effluent	2.19 g P/m ³

The next pages show the main results of the calibrated model, concerning the influent and output streams characterisation. A more detailed table containing data from all the process streams can be found in the appendix (Appendix IV – Simulation Results).

- Wastewater influent (before the addition of urea)

Table 36- Wastewater influent characterisation - main parameters.

Flow:	46,282 (m ³ /d) (on the 80 th day of the simulation)		
Total COD:	1,095.68 g O ₂ /m ³	Metal hydroxides:	79.6 g/m ³
Soluble COD:	908.85 g O ₂ /m ³	S_I:	252 g COD/m ³
Particulate COD:	187.13 g O ₂ /m ³	S_F:	405 g COD/m ³
BOD₅:	315.36 g O ₂ /m ³	S_{LF}:	252 g COD/m ³
Alkalinity:	350 g CaCO ₃ /m ³	X_I:	142 g COD/m ³
TSS:	250 g/m ³	X_S:	43.8 g COD/m ³
VSS:	127.50 g/m ³	TKN - as free and ionized ammonia	4.0 g N/m ³
Total inorganic solids:	122.50 g/m ³	Total phosphorus - as orthophosphate	5.7 g P/m ³

- Urea influent

Table 37 - Urea influent characterisation - main parameters

Flow:	0.29 (m ³ /d) (constant flow)		
Total COD:	117.00 g O ₂ /m ³	Total inorganic solids:	0.49 g/m ³
Soluble COD:	99.45 g O ₂ /m ³	S_I:	99.5 g COD/m ³
Particulate COD:	17.55 g O ₂ /m ³	S_F:	0 g COD/m ³
BOD₅:	1.54 g O ₂ /m ³	S_{LF}:	0 g COD/m ³
Alkalinity:	350 g CaCO ₃ /m ³	X_I:	15.2 g COD/m ³
TSS:	1.95 g/m ³	X_S:	2.34 g COD/m ³
VSS:	1.46 g/m ³	TKN - as free and ionized ammonia	231,000 g N/m ³

- Aeration tank (output stream – ml)

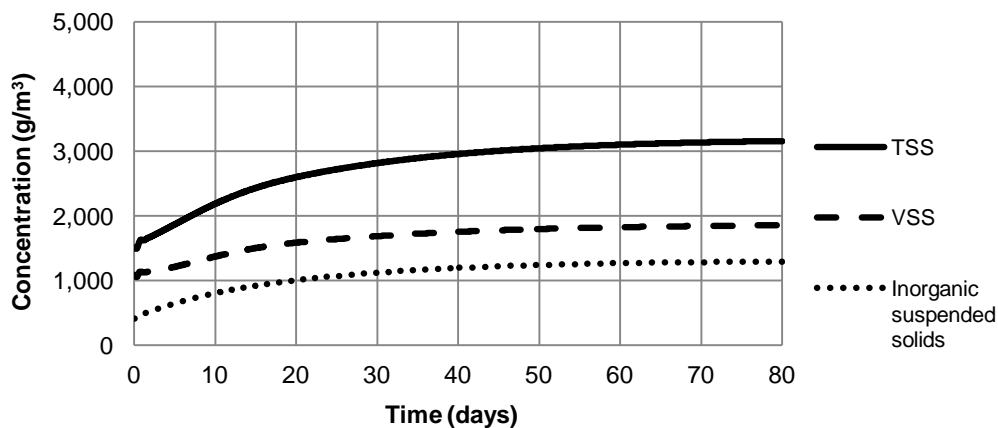


Figure 13 - Evolution of the solids in the aeration tank during the 80 days of simulation.

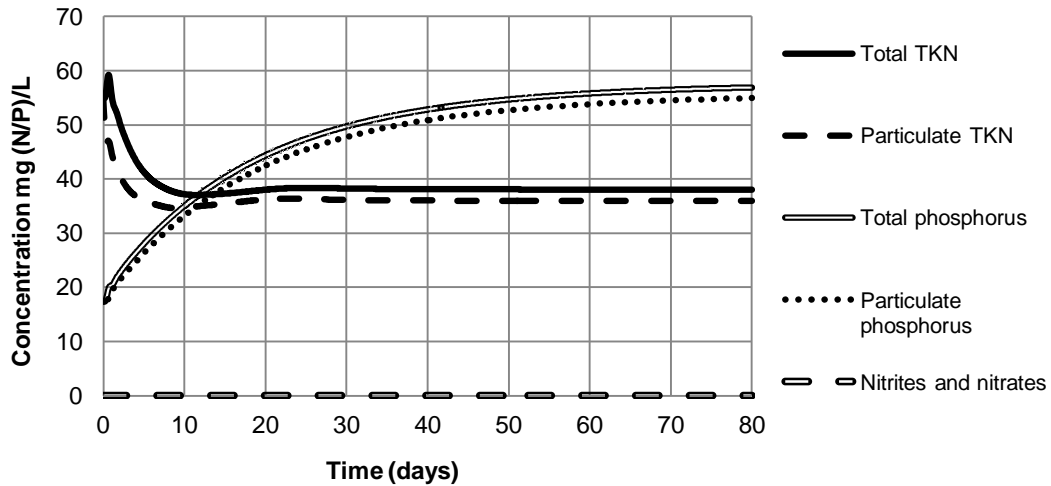


Figure 14 - Evolution of the nutrients in the aeration tank during the 80 days of simulation.

As shown in Figure 14, the TKN and total phosphorus are mostly found in the particulate form, i.e., associated with the biological sludge – biomass. Concerning the phosphorus profile, since there are no anaerobic sections in the aeration tank, the phosphorus – orthophosphate is mainly removed via chemical precipitation.

In terms of TKN, which is assumed as ammonia, it only serves as nitrogen supply for synthesis of heterotrophic bacteria since the autotrophic biomass was considered to be zero in the modelling. Therefore, TKN is only consumed for heterotrophic growth during the entire simulation. Also, as there is no autotrophic biomass there is no nitrification and no nitrites or nitrates are produced.

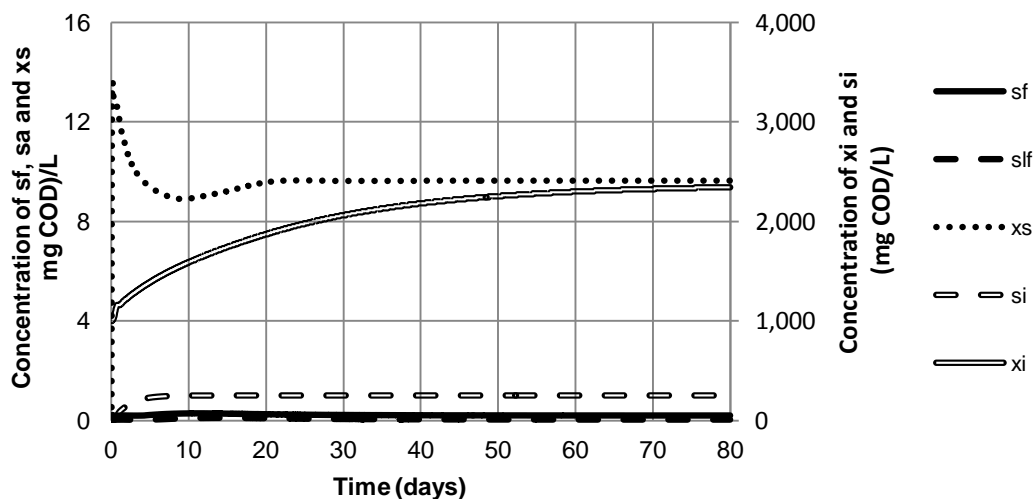


Figure 15 - Evolution of soluble and particulate material in the aeration tank during the 80 days of simulation.

For what concerns the output stream (ml) in terms of particulate and soluble material, the soluble components sf and slf decrease during the simulation, as they are the substrates used for biomass growth. The soluble inert material stays approximately the same during the entire simulation, as it is not consumed or created. The slowly biodegradable substrate diminishes once it is hydrolysed and converted to readily biodegradable substrate. Beyond that, there is a significant increase in the inert particulate material due to metal precipitation.

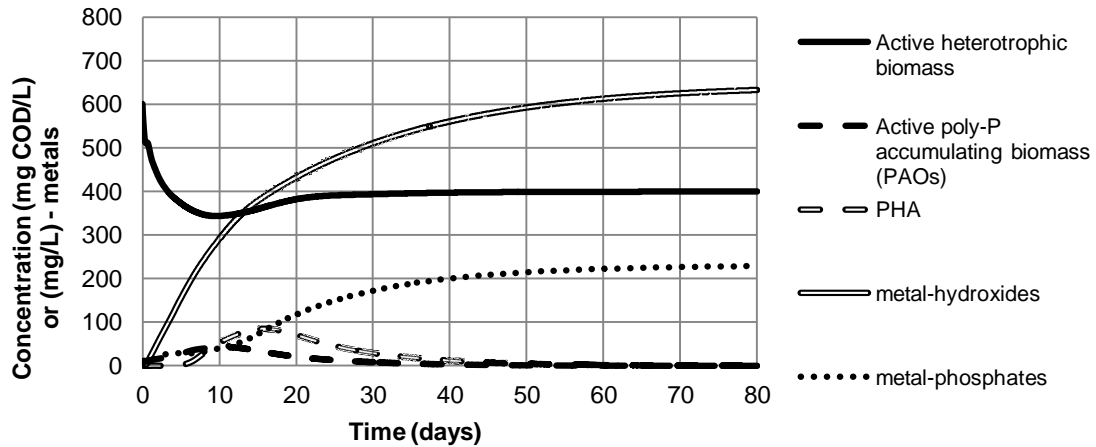


Figure 16 - Evolution of biomass, PHA and metals in the aeration tank during the 80 days of simulation.

From the analysis of Figure 16, it is noticed a significant drop of the heterotrophic biomass in the first days of simulation. This is not due to a decay phenomenon but to the initial input concentration of heterotrophic biomass in the tank (600 mg COD/L), which was overestimated. In the reality the heterotrophic biomass should follow steady-state behaviour where the biomass growth is balanced by biomass lysis and decay. As for the metal-phosphates, their concentration increases over time due to the chemical precipitation of phosphorus. The metal-hydroxides are the component associated with the largest increase over the simulation, which reinforces the idea of a considerable calcium precipitation during the biological process.

- Aeration tank (inside the tank)

Table 38 - Dissolved oxygen (DO) and alkalinity profile inside the aeration tank (average values).

Average values								
Parameter:	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
DO (g O ₂ /m ³) obtained by the simulation	0.59	0.65	2.31	3.17	3.16	3.07	3.43	3.38
DO (g O₂/m³) Portucel's historical data	0.50 ± 0.16	0.40 ± 0.16	2.70 ± 0.63	3.30 ± 0.65	3.60 ± 0.79	3.20 ± 0.95	3.70 ± 0.98	3.80 ± 0.94
Alkalinity (g CaCO ₃ /m ³) obtained by the simulation	436.15	446.02	469.46	493.33	513.19	529.44	541.09	547.35

The oxygen is mostly consumed in the first sections of the aeration tank, where the concentration of bCOD is bigger. The increase in DO along the tank is consistent with the trend observed experimentally, and suggests a much smaller oxygen consumption in the last half of the tank, perhaps due to the elimination of most of the bCOD by this stages. For what concerns the alkalinity, the growth of biomass is associated with the production of carbon dioxide which consequently affects the alkalinity of the wastewater.

- Clarifiers

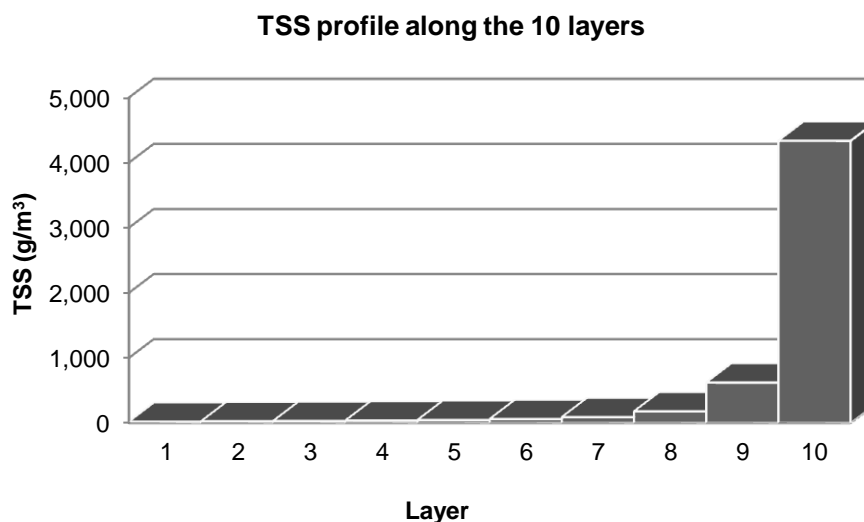


Figure 17 - TSS profile along the 10 layers (average values).

As can be seen in Figure 17, the clarification is conducted in a very efficient way as the TSS profile along the layers describe a minimum concentration in the majority of the layers and the highest concentration at the bottom layer.

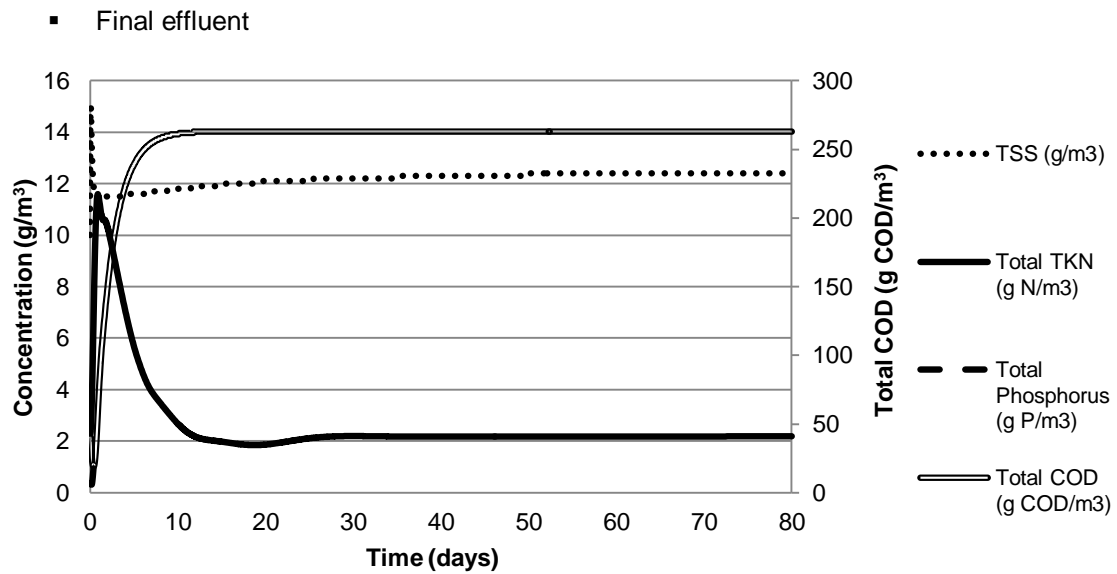


Figure 18 - Evolution of the main output parameters of the final effluent during the 80 days of simulation.

Regarding the final effluent, during the first days of the simulation, an increase of the majority of the parameters is noticed, since the system has not yet reached the steady state. From day 10 until the last day of the simulation, the parameters stay approximately constant.

Overall, only minor differences between the WWTP's historical data and the results from model simulations were observed, thus, the calibration of the target parameters was successfully achieved, and both the influent and effluent streams were well characterized.

CHAPTER 5. CASE STUDY: UREA

Once the calibration of the model was completed, it could finally be used to predict the system response to a certain modification in operation, and consequently find the best strategies that lead to process optimization and control. In this study there was an interest in studying the effect of the urea addition to the influent. The urea addition has no precise control in the WWTP of Portucel: it is conducted by means of a pump that, in normal conditions, debits a constant flowrate of $0.29 \text{ m}^3/\text{d}$. This value was not subjected to careful study since the ATF paper mill started to operate. The increase/decrease of the flowrate is only regulated in case of a pump malfunction or an excessive increase of the incoming influent. Besides, $0.29 \text{ m}^3/\text{d}$ comprises a very small fraction of the influent ($46,918 \text{ m}^3/\text{d}$) which suggests that this tiny flowrate may not even be necessary in the operation of the process and it may not be a critical variable in the WWTP's performance.

In order to study this situation, the subsequent strategy was followed: a series of simulations were conducted, by changing only the flowrate of the urea influent and observing the changes in the main streams of the biological treatment; from these results, the urea flowrate was decreased to half the normal value, by decreasing the frequency of the feeding pump, at Portucel. After a period of about 20 days the dehydrated sludge was weighed. The results from the simulations (Table 39) and validation (Table 40) are shown below:

Simulations:

Table 39 - Simulation results for the urea flowrate decrease (after a 80 day period).

Urea Flowrate (m^3/d)	0.29	0.2	0.15	0.08	0
TSS in the aeration tank (g/m^3)	3,154	3,156	3,158	3,160	3,162
TKN in the aeration tank ($\text{g N}/\text{m}^3$)	38.03	37.88	37.82	37.73	37.62
Sludge production (kg/d)	12,493	12,503	12,508	12,515	12,523
TSS in the final effluent (g/m^3)	12.42	12.42	12.42	12.42	12.43
TKN in the final effluent ($\text{g N}/\text{m}^3$)	2.20	1.66	1.36	0.95	0.47
Total COD in the effluent ($\text{g COD}/\text{m}^3$)	262.92	263.00	263.08	263.21	263.45

It was expected that the decrease of the urea flowrate would be associated with a decrease in the TSS and sludge production in the overall process: the presence of less ammonia in the mixed liquor would translate in a more limited growth of heterotrophic biomass and as a result

the sludge production would be lower. However, the results from the simulations (see **Table 39**) show that the most direct effect of the reduction of the urea flowrate is the decrease of the concentration of TKN in the final effluent, which was also theoretically expected. For what concerns the sludge production, it seems to increase with the sequential decrease of the urea flowrate. Nonetheless, this increase is not very significant. On the other hand, the final effluent is not disturbed for what concerns the TSS and total COD – the WWTP's performance is not affected, even in the case of the complete elimination of the addition of urea. Furthermore, the decrease of the concentration of TKN in the final effluent would also reduce even more the potential of eutrophication when the wastewater is discharged in the Sado River.

Validation at Portucel:

Table 40 - Summary of results concerning the urea flowrate experiment at Portucel.

Sludge weighing experiment:	Date:	Urea flowrate (m³/d):	Dehydrated sludge production (kg/h)	Sludge consistency (%)
1	15-04-2014	0.29	16,008.00	11.5
2	06-05-2014	0.29	20,454.72	14.9
3	05-08-2014	0.15	14,230.08	12.2

The quantification of biological sludge production was not a usual procedure in Portucel's WWTP. Therefore, the first and second sludge weighing experiments were carried out as an attempt to quantify the biological sludge production, by counting the time that it took for a 10 ton trailer to be full of sludge coming from the dewatering filter press. These two experiments were carried out long before the start of the urea flowrate decrease experiment and as can be seen, the results obtained for the dehydrated sludge production are quite different between the two measurements. This is mainly due to the dynamic consistency of the dehydrated sludge. As it was mentioned in Portucel's WWTP – description (Chapter 3), the excess sludge (biological sludge) is gathered with the sludge that comes from the PPS, in the thickener. Therefore, the resulting dehydrated sludge will depend not only on the consistency of the biological sludge from the activated sludge WWTP but also on the consistency and flowrate of the biological sludge coming from PPS's SBR.

As shown in Table 40, the third sludge weighing, which is related to the dehydrated sludge production 20 days after the start of the urea flowrate decrease, resulted in a lower value of sludge production. However, the difference between the three values is not significant enough to effectively conclude that it is related to a lower or higher heterotrophic growth of biomass. In order to obtain a final conclusion, more experimental weightings should be done. Also, the dehydrated sludge production should be complemented with nitrogen measurements to the treated effluent, in order to confirm if the nitrogen content lowered after the start of the urea flowrate decrease experiment, as indicated by the simulations shown in Table 39.

CHAPTER 6. CONCLUSIONS AND FUTURE DEVELOPMENTS

The modelling of wastewater treatment plants is increasingly a reality and not just a laboratory-scale project. It offers clear advantages in terms of analyzing the performance of the treatment plant as well as better optimization and control tools, reducing the costs associated with laboratory analysis. Nevertheless, the efficiency of modelling depends on a good calibration, which is generally needed to adapt the simulation results to the real behaviour of the WWTP. There have been a lot of studies about the modelling of municipal WWTPs but there still are very few concerning the modelling of industrial WWTPs. Therefore, it was the purpose of this study to address the modelling of a pulp and paper mill wastewater treatment plant.

The effluent from this industry has a high chemical oxygen demand and a considerably low biochemical oxygen demand, which shows a low ratio of biodegradability of the effluent (only about 30% is biodegradable). It is rich in fibers, starch, lignin and its derivatives, resin acids and chlorinated and sulphur compounds. The treatment process is based on the activated sludge process and the treated effluent is discharged in the Sado river with excellent characteristics in terms of COD, SST and nutrients removal.

The modelling of Portucel's WWTP was achieved with the help of the commercial software GPS-X, more specifically, using the model ASM2d for modelling carbonaceous oxidation, nitrification, denitrification and biological and chemical phosphorus removal. The latter presented a significant interest for this study since it was also associated with the chemical precipitation of metals, namely in the form of metal phosphates. The denitrification step was not important for the modelling as there are no anaerobic or anoxic unit processes in Portucel's WWTP. The design of the WWTP in GPS-X involved not only the collection of physical data concerning the unit processes but also the collection of historical data about the WWTP performance over the last three years. The historical data allowed calculating the input parameters of the model, instead of proceeding to intensive measurement campaign collecting, based on batch tests analysis, which is an expensive and long lasting procedure.

Regarding the input parameter estimation, the first attempt of estimating the organic fractions was not successful, due to an error in data reconciliation. It is believed that this error is associated with an inappropriate estimation of particulate COD, namely in terms of the slowly biodegradable substrate fraction. Therefore, a sensitivity analysis was done, which allowed understanding that the inert particulate and slowly biodegradable substrate fractions of the influent's COD have an important role in achieving a good fitting of the model. This fact suggests that the pulp and paper effluent has a considerable amount of inert particulate and substances, probably not only metals but also significant lignin content. The volatile fatty acids

present in the influent are also considerably high. Finally, it was also necessary to adjust the initial concentrations and the nutrient fractions of the influent: the occurrence of an excessive nitrification was verified and therefore the autotrophic organisms were eliminated from the model as well as the nitrogen content of most of the organic fractions. This procedure allowed minimizing the nitrates and nitrites in the final effluent and also the nitrogen content of the sludge. In this study it was chosen not to change the stoichiometric and kinetic parameters, since this would involve a better understanding of the kinetic of the overall process and also the formulation of several batch tests. Furthermore, the sensitivity analysis showed that extreme changes in parameters did not significantly improve the model prediction.

As for the urea case study, the simulation results showed that the adding of urea has no considerable effect on the efficiency of the biological process, namely in the COD removal. Besides, the elimination of urea would cause a lower concentration of nitrogen in the final effluent, which diminishes the quantity of nitrogen dumped to the river. The validation of this study at the WWTP, though the decrease of the urea flowrate to half the usual value, translated in a less sludge production, although this difference was not significant enough to precise that it was related to a less biomass growth. Despite this fact, it was concluded that the addition of urea is no longer needed.

As future developments of this study, it would be useful to elaborate some batch tests based on respirometry with the purpose of estimating the true value of bCOD. These tests should also be performed at different temperatures and F/M ratios in order to study the yield and kinetic parameters and therefore have a better knowledge of the influent and nutrient fractions. Despite their effort and cost, batch tests are important in a higher stage of this study in order to validate the calibration.

It would also be interesting to study, through analytical methods, the content of lignin in the wastewater influent in order to evaluate its influence on the particulate inert material.

The modelling of this WWTP with different models, e.g. ASM3, TUDP and Mantis2 would also be interesting as a future development, mainly with the intention of finding the model that characterizes better the behaviour of the WWTP.

Lastly, the complete elimination of urea at Portucel's WWTP would be an interesting experiment to follow, since it would validate, in a more comprehensive way, the conclusions that were withdrawn previously.

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APPENDIX

Appendix I – ASM2d rate equations

Hydrolysis:

Table 41 – ASM2d rate equations for hydrolysis. Source: M. Henze et al. [28]

Process:	Rate equation:
Aerobic Hydrolysis	$K_H \times \frac{S_O}{K_{O_2} + S_O} \times \frac{\frac{X_S}{X_{BH}}}{K_X + \frac{X_S}{X_{BH}}} \times X_{BH}$
Anoxic Hydrolysis	$K_H \times \eta_{NO_3} \times \frac{K_{O_2}}{K_{O_2} + S_O} \times \frac{S_{NO}}{K_{NO_3} + S_{NO}} \times \frac{\frac{X_S}{X_{BH}}}{K_X + \frac{X_S}{X_{BH}}} \times X_{BH}$
Anaerobic Hydrolysis	$K_H \times \eta_{fe} \times \frac{K_{O_2}}{K_{O_2} + S_O} \times \frac{K_{NO_3}}{K_{NO_3} + S_{NO}} \times \frac{\frac{X_S}{X_{BH}}}{K_X + \frac{X_S}{X_{BH}}} \times X_{BH}$

Label: K_H – Hydrolysis rate constant (d^{-1}); K_{O_2} – Saturation/inhibition coefficient for oxygen ($g\ O_2 \cdot m^{-3}$); K_X – Saturation/inhibition coefficient for particulate COD ($g\ X_S \cdot g^{-1}\ X_H$); K_{NO_3} – Saturation/inhibition coefficient for nitrate ($g\ N \cdot m^{-3}$); η_{NO_3} – Anoxic hydrolysis reduction factor; η_{fe} – Anaerobic hydrolysis reduction factor.

Processes concerning heterotrophic organisms (X_{BH}):

Table 42 – AM2d rate equations for processes concerning heterotrophic organisms. Source: M. Henze et al. [28]

Process:	Rate equation:
Growth on fermentable substrates (S_F)	$\mu_H \times \frac{S_O}{K_{O_2} + S_O} \times \frac{S_F}{K_F + S_F} \times \frac{S_F}{S_F + S_{LF}} \times \frac{S_{NH}}{K_{NH} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BH}$
Growth on fermentation products (S_{LF})	$\mu_H \times \frac{S_O}{K_{O_2} + S_O} \times \frac{S_{LF}}{K_{LF} + S_{LF}} \times \frac{S_{LF}}{S_F + S_{LF}} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BH}$
Denitrification with fermentable substrates (S_F)	$\mu_H \times \eta_g \times \frac{K_{O_2}}{K_{O_2} + S_O} \times \frac{S_{NO}}{K_{NO_3} + S_{NO}} \times \frac{S_F}{K_F + S_F} \times \frac{S_F}{S_F + S_{LF}} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BH}$
Denitrification with fermentation products (S_{LF})	$\mu_H \times \eta_g \times \frac{K_{O_2}}{K_{O_2} + S_O} \times \frac{S_{NO}}{K_{NO_3} + S_{NO}} \times \frac{S_{LF}}{K_{LF} + S_{LF}} \times \frac{S_{LF}}{S_F + S_{LF}} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BH}$
Fermentation	$q_{fe} \times \frac{K_{O_2}}{K_{O_2} + S_O} \times \frac{K_{NO_3}}{K_{NO_3} + S_{NO}} \times \frac{S_F}{K_{Fe} + S_F} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BH}$
Lysis	$b_H \times X_{BH}$

Label: μ_H – Maximum growth rate on substrate ($g X_S \cdot g^{-1} X_H \cdot d^{-1}$); K_{O_2} – Saturation/inhibition coefficient for oxygen ($g O_2 \cdot m^{-3}$); K_F – Saturation coefficient for growth on S_F ($g COD \cdot m^{-3}$); K_{NH_4} – Saturation coefficient for ammonium (nutrient) ($g N \cdot m^{-3}$); K_P – Saturation coefficient for phosphate (nutrient) ($g P \cdot m^{-3}$); K_{ALK} – Saturation coefficient for alkalinity (HCO_3^-) (mole $HCO_3^- \cdot m^{-3}$); K_{LF} – Saturation coefficient for growth on acetate S_{LF} ($g COD \cdot m^{-3}$); $K_{NO_3^-}$ – Saturation/inhibition coefficient for nitrate ($g N \cdot m^{-3}$); $\eta_{NO_3^-}$ – Reduction factor for denitrification; K_{fe} – Saturation coefficient for fermentation of S_F ($g COD \cdot m^{-3}$); q_{fe} – Maximum rate for fermentation ($g S_F \cdot g^{-1} X_H \cdot d^{-1}$); b_H – Rate constant for lysis and decay (d^{-1});

Phosphorus accumulating organisms (X_{BP}):

Table 43 –ASM2d rate equations for processes concerning phosphorus accumulating organisms (PAO). Source: M. Henze et al. [28]

Process:	Rate equation:
Storage of X_{PHA}	$q_{PHA} \times \frac{S_{LF}}{K_{LF} + S_{LF}} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times \frac{\frac{X_{PP}}{X_{BP}}}{K_{PP} + \frac{X_{PP}}{X_{BP}}} \times X_{BP}$
Aerobic storage of X_{PP}	$q_{PP} \times \frac{S_0}{K_{O_2} + S_0} \times \frac{S_P}{K_{PS} + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times \frac{\frac{X_{BT}}{X_{BP}}}{K_{PHA} + \frac{X_{BT}}{X_{BP}}} \times \frac{K_{MAX} - \frac{X_{PP}}{X_{BP}}}{K_{IPP} + K_{MAX} - \frac{X_{PP}}{X_{BP}}} \times X_{BP}$
Anoxic storage of X_{PP}	$q_{PP} \times \frac{S_0}{K_{O_2} + S_0} \times \frac{S_P}{K_{PS} + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times \frac{\frac{X_{BT}}{X_{BP}}}{K_{PHA} + \frac{X_{BT}}{X_{BP}}} \times \frac{K_{MAX} - \frac{X_{PP}}{X_{BP}}}{K_{IPP} + K_{MAX} - \frac{X_{PP}}{X_{BP}}} \times X_{BP} \times \eta_{NO_3} \times \frac{K_{O_2}}{S_0} \times \frac{S_{NO}}{K_{NO_3} + S_{NO}}$
Aerobic growth on X_{PHA}	$\mu_{PAO} \times \frac{S_0}{K_{O_2} + S_0} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times \frac{\frac{X_{BT}}{X_{BP}}}{K_{PHA} + \frac{X_{BT}}{X_{BP}}} \times X_{BP}$
Anoxic growth on X_{PHA}	$\mu_{PAO} \times \frac{S_0}{K_{O_2} + S_0} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times \frac{\frac{X_{BT}}{X_{BP}}}{K_{PHA} + \frac{X_{BT}}{X_{BP}}} \times X_{BP} \times \eta_{NO_3} \times \frac{K_{O_2}}{S_0} \times \frac{S_{NO}}{K_{NO_3} + S_{NO}}$
Lysis of X_{PAO}	$b_{PAO} \times X_{BP} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}}$
Lysis of X_{PP}	$b_{PP} \times X_{PP} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}}$
Lysis of X_{PA}	$b_{PHA} \times X_{BT} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}}$

Label: q_{PHA} – Rate constant for storage of X_{PHA} (base X_{PP}) ($g\ X_{BT} \cdot g^{-1}\ X_{BP} \cdot d^{-1}$); K_{LF} - Saturation coefficient for growth on acetate S_{LF} ($g\ COD \cdot m^{-3}$); K_{ALK} - Saturation coefficient for alkalinity (HCO_3^-) (mole $HCO_3^- \cdot m^{-3}$); K_{PP} - Saturation coefficient for poly-phosphate ($g\ X_{PP} \cdot g^{-1}\ X_{BP}$); q_{PP} – Rate constant for storage of X_{PP} (base X_{PP}) ($g\ X_{PP} \cdot g^{-1}\ X_{BP} \cdot d^{-1}$); K_{O_2} – Saturation/inhibition coefficient for oxygen ($g\ O_2 \cdot m^{-3}$); K_{PS} - Saturation coefficient for phosphorus in storage of PP ($g\ P \cdot m^{-3}$); K_{ALK} - Saturation coefficient for alkalinity (HCO_3^-) (mole $HCO_3^- \cdot m^{-3}$); K_{PHA} – Saturation coefficient for PHA ($g\ X_{BT} \cdot g^{-1}\ X_{BP}$); K_{MAX} – Maximum ratio of X_{PP}/X_{BP} ($g\ X_{PP} \cdot g^{-1}\ X_{BP}$); K_{IPP} - Inhibition coefficient for PP storage ($g\ X_{PP} \cdot g^{-1}\ X_{BP}$); K_{NO_3} – Saturation/inhibition coefficient for nitrate ($g\ N \cdot m^{-3}$); η_{NO_3} – Reduction factor for anoxic activity; μ_{PAO} – Maximum growth rate of PAO (d^{-1}); K_{NH_4} - Saturation coefficient for ammonium (nutrient) ($g\ N \cdot m^{-3}$); b_{PAO} – Rate for lysis of X_{BP} (d^{-1}); b_{PP} – Rate for lysis of X_{PP} (d^{-1}); b_{PHA} – Rate for lysis of X_{BT} (d^{-1});

Nitrifying organisms (autotrophic organisms X_{BA}):

Table 44 – ASM2d rate equations for processes concerning nitrifying organisms (autotrophic organisms). Source: M. Henze et al. [28]

Process:	Rate equation:
Aerobic growth of X_{AUT}	$\mu_{AUT} \times \frac{S_0}{K_{O_2} + S_0} \times \frac{S_{NH}}{K_{NH_4} + S_{NH}} \times \frac{S_P}{K_P + S_P} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \times X_{BA}$
Lysis of X_{AUT}	$b_{AUT} \times X_{BA}$

Label: μ_{AUT} – Maximum growth rate of X_{BA} (d^{-1}); K_{O_2} – Saturation/inhibition coefficient for oxygen ($g\ O_2 \cdot m^{-3}$); K_A – Saturation coefficient for ammonium (substrate) ($g\ N \cdot m^{-3}$); K_P – Saturation coefficient for phosphate (nutrient) ($g\ P \cdot m^{-3}$); K_{ALK} – Saturation coefficient for alkalinity (HCO_3^-) (mole $HCO_3^- \cdot m^{-3}$); b_{AUT} – Decay rate of X_{BA} (d^{-1})

Simultaneous precipitation of phosphorus with ferric hydroxide:

Table 45 – ASM2d rate equations for simultaneous precipitation of phosphorus with ferric hydroxide. Source: M. Henze et al. [28]

Process:	Rate equation:
Precipitation	$k_{PRE} \times S_P \times X_{MeOH}$
Redissolution	$k_{RED} \times X_{MeP} \times \frac{S_{ALK}}{K_{ALK} + S_{ALK}}$

Label: k_{PRE} – Rate constant for P precipitation ($m^3 \cdot g^{-1}\ Fe(OH)_3 \cdot d^{-1}$); k_{RED} – Rate constant for redissolution (d^{-1}). K_{ALK} – Saturation coefficient for alkalinity (HCO_3^-) (mole $HCO_3^- \cdot m^{-3}$);

Table 46 - Definition and typical values for the kinetic parameters of ASM2d.
Source: M. Henze et al. [28]

Kinetic parameter:		20°C	10°C	Units
K_H	Hydrolysis rate constant	3.00	2.00	d^{-1}
η_{NO_3}	Anoxic hydrolysis reduction factor	0.60	0.60	-
η_{fe}	Anaerobic hydrolysis reduction factor	0.40	0.40	-
K_{O_2}	Saturation/inhibition coefficient for oxygen	0.20	0.20	$g\ O_2\ m^{-3}$
K_{NO_3}	Saturation/inhibition coefficient for nitrate	0.50	0.50	$g\ N\ m^{-3}$
K_X	Saturation/inhibition coefficient for particulate COD	0.10	0.10	$g\ X_S\ g^{-1}\ X_H$
μ_H	Maximum growth rate on substrate	6.00	3.00	$g\ X_S\ g^{-1}\ X_H\ d^{-1}$
q_{fe}	Maximum rate for fermentation	3.00	1.50	$g\ S_F\ g^{-1}\ X_H\ d^{-1}$
η_g	Reduction factor for denitrification	0.80	0.80	-
b_H	Rate constant for lysis and decay	0.40	0.20	d^{-1}
K_F	Saturation coefficient for growth on S_F	4.00	4.00	$g\ COD\ m^{-3}$
K_{fe}	Saturation coefficient for fermentation on S_F	4.00	4.00	$g\ COD\ m^{-3}$
K_{LF}	Saturation coefficient for growth on S_{LF}	4.00	4.00	$g\ COD\ m^{-3}$
K_{NH_4}	Saturation coefficient for ammonia (nutrient)	0.05	0.05	$g\ N\ m^{-3}$
K_P	Saturation coefficient for phosphate	0.01	0.01	$g\ P\ m^{-3}$
K_{ALK}	Saturation coefficient for alkalinity	0.10	0.10	$mole\ HCO_3^-\ m^{-3}$
q_{PHA}	Rate constant for storage of X_{BT}	3.00	2.00	$g\ X_{BT}\ g^{-1}\ X_{BP}\ d^{-1}$
q_{PP}	Rate constant for storage of X_{PP}	1.50	1.00	$g\ X_{PP}\ g^{-1}\ X_{BP}\ d^{-1}$
μ_{PAO}	Maximum growth rate of PAO	1.00	0.67	d^{-1}
b_{PAO}	Rate for lysis of X_{BP}	0.20	0.10	d^{-1}
b_{PP}	Rate for lysis of X_{PP}	0.20	0.10	d^{-1}
b_{PHA}	Rate for lysis of X_{PHA}	0.20	0.10	d^{-1}
K_{PS}	Saturation coefficient for phosphorus in storage of PP	0.20	0.20	$g\ P\ m^{-3}$
K_{PP}	Saturation/ coefficient for poly-phosphate	0.01	0.01	$g\ X_{PP}\ g^{-1}\ X_{BP}$
K_{MAX}	Maximum ratio of X_{PP}/X_{BP}	0.34	0.34	$g\ X_{PP}\ g^{-1}\ X_{BP}$
K_{IPP}	Inhibition coefficient for PP storage	0.02	0.02	$g\ X_{PP}\ g^{-1}\ X_{BP}$
K_{PHA}	Saturation coefficient for PHA	0.01	0.01	$g\ X_{PHA}\ g^{-1}\ X_{BP}$
μ_{AUT}	Maximum growth rate of X_{BA}	1.00	0.35	d^{-1}
b_{AUT}	Decay rate of X_{BA}	0.15	0.05	d^{-1}
K_A	Saturation coefficient for ammonia (substrate)	1.00	1.00	$g\ N\ m^{-3}$
k_{PRE}	Rate constant for P precipitation	1.00	1.00	$m^3\ g^{-1}\ Fe(OH)_3\ d^{-1}$
k_{RED}	Rate constant for redissolution	0.60	0.60	d^{-1}

Table 47 - ASM2d model stoichiometry. Source: M. Henze et al. [28]

Stoichiometric parameters:		Value:	Units:
Hydrolysis			
f_{SI}	Production of SI in hydrolysis	0	$\text{g COD g}^{-1} \text{COD}$
Heterotrophic biomass (X_{BH})			
Y_H	Yield coefficient	0.625	$\text{g COD g}^{-1} \text{COD}$
f_{XI}	Fraction of inert COD generated in biomass lysis	0.10	$\text{g COD g}^{-1} \text{COD}$
Phosphorus accumulating organisms (X_{BP})			
Y_{PAO}	Yield coefficient (biomass/PHA)	0.625	$\text{g COD g}^{-1} \text{COD}$
Y_{PO4}	PP requirement (PO_4 release) per PHA stored	0.40	$\text{g P g}^{-1} \text{COD}$
Y_{PHA}	PHA requirement for PP storage	0.20	$\text{g COD g}^{-1} \text{P}$
Nitrifying organisms (X_{BA})			
Y_A	Yield of autotrophic biomass per NO_3^- -N	0.24	$\text{g COD g}^{-1} \text{N}$

Appendix II – Composite Variables

BOD, COD and TSS Composite Variables

Table 48 - BOD, COD and TSS composite variables for ASM2d. Source: GPS-X Technical Reference [31]

	sbodu	xbodu	bodu	sbod	xbod	bod	scod	xcod	cod	vss	xiss	x
ss	1		1	fbod		fbod	1		1			
sf	1		1	fbod		fbod	1		1			
slf	1		1	fbod		fbod	1		1			
xs		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xbh		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xba		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xbp		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
si							1		1			
xi								1	1	icv ⁻¹		icv ⁻¹
xu								1	1	icv ⁻¹		icv ⁻¹
xgly		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xbt		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xsto		1	1		fbod	fbod		1	1	icv ⁻¹		icv ⁻¹
xii											1	1
xmeoh											1	1
xmep											1	1
xpp											3	3
xppr											3	3

fbod and icv: see Table 19

Nitrogen Composite Variables

Table 49 – Nitrogen Composite Variables.Source: GPS-X Technical Reference [31]

	stkn	xtkn	tkn	tn
sno				1
snh	1		1	1
sni	1		1	1
snd	1		1	1
xnd		1	1	1
si	insi		insi	insi
sf	insf		insf	insf
xbp		inbm	inbm	inbm
xbh		inbm	inbm	inbm
xba		inbm	inbm	inbm
xi		inxi	inxi	inxi
xs		inxs	inxs	inxs

insi, insf, inbm, inxi and inxm: see Table 21

Phosphorus Composite Variables

Table 50 - Phosphorus composite variables. Source: GPS-X Technical Reference [31]

	stp	xtp	tp
sp	1		1
sf	ipsf		ipsf
si	ipsi		ipsi
xi		ipxi	ipxi
xs		ipxs	ipxs
xbh		ipbm	ipbm
xba		ipbm	ipbm
xbp		ipbm	ipbm
xmep		0.205	0.205
xpp		1	1
xppr		1	1

ipsi, ipsf, ipbm, ipxi and ipxm: see Table 21

Appendix III – BOD₅:N:P ratios

Table 51 - Nutrient Ratios registered in the WWTP's influent over the last 3 years.

Year	Month	Influent Flowrate (m ³ /d)	BOD ₅ (kg O ₂)	N (kg)	P (kg)	Ratio BOD ₅ :N	Ratio BOD ₅ :P
2011	January	45,143.03	10,157.18	248.77	322.01	40.83	31.54
	February	46,721.93	16,352.68	257.47	236.41	63.51	69.17
	March	45,410.00	15,893.50	250.24	194.09	63.51	81.89
	April	43,467.22	14,344.18	239.53	212.79	59.88	67.41
	May	46,247.58	15,261.70	254.85	503.79	59.88	30.29
	June	43,849.19	17,101.18	241.64	349.50	70.77	48.93
	July	43,266.26	9,258.98	238.43	185.93	38.83	49.80
	August	43,233.55	9,943.72	238.24	155.75	41.74	63.84
	September	46,652.13	11,896.29	257.08	351.16	46.27	33.88
	October	44,561.03	10,694.65	245.56	321.39	43.55	33.28
	November	45,757.30	11,439.33	252.15	232.12	45.37	49.28
	December	43,106.26	9,483.38	237.54	304.40	39.92	31.15
2012	January	39,522.26	10,275.79	217.79	202.96	47.18	50.63
	February	39,524.55	8,695.40	217.81	205.57	39.92	42.30
	March	40,540.52	13,378.37	223.40	318.02	59.88	42.07
	April	41,686.47	12,922.80	229.72	177.89	56.25	72.64
	May	38,497.61	11,164.31	212.15	199.60	52.63	55.93
	June	39,067.53	13,282.96	215.29	236.06	61.70	56.27
	July	38,993.32	10,918.13	214.88	252.25	50.81	43.28
	August	39,669.23	11,107.38	218.60	181.04	50.81	61.35
	September	39,826.87	18,320.36	219.47	284.62	83.47	64.37
	October	39,658.00	9,517.92	218.54	270.22	43.55	35.22
	November	38,713.33	no data	213.34	143.70	no data	no data
	December	38,397.87	11,519.36	211.60	160.74	54.44	71.67
2013	January	39,405.13	14,579.90	217.15	296.84	67.14	49.12
	February	42,591.50	16,184.77	234.71	275.78	68.96	58.69
	March	38,703.16	12,385.01	213.28	162.56	58.07	76.19
	April	40,729.20	14,662.51	224.44	164.44	65.33	89.16
	May	40,578.26	10,550.35	223.61	354.16	47.18	29.79
	June	40,504.20	13,771.43	223.20	193.93	61.70	71.01
	July	41,023.65	13,402.40	226.07	163.20	59.29	82.12
	August	41,057.58	10,674.97	226.25	215.64	47.18	49.50
	September	41,813.87	14,634.85	230.42	222.97	63.51	65.64
	October	43,536.29	12,190.16	239.91	124.47	50.81	97.93
	November	41,759.10	14,198.09	230.12	261.29	61.70	54.34
	December	41,681.55	11,670.83	229.69	182.91	50.81	63.81
Overall average						54.75	56.39

Appendix IV – Simulation Results

Table 52 - Simulation Results - streams characterisation on the 80th day of the simulation - Part I.

		urea	inf0	inf	ml(1)	ml(2)	ml(3)
Flow	m ³ /d	0.29	41,874.97	41,875.26	-	-	-
TSS	g/m ³	1.95	250.00	250.00	2,725.19	3,152.70	3,154.54
	kg/d	5.66E-04	10,468.74	10,468.74	-	-	-
VSS	g/m ³	1.46	127.50	127.50	1,603.63	1,857.89	1,859.81
Soluble BOD₅	g O ₂ /m ³	0.00	282.51	282.51	156.52	104.16	83.42
BOD₅	g O ₂ /m ³	1.54	301.34	301.34	410.09	391.51	369.61
Soluble COD	g COD/m ³	99.45	908.85	908.84	489.00	409.67	378.25
COD	g COD/m ³	117.00	1,095.00	1,094.99	2,862.37	3,159.34	3,130.76
	kg/d	0.03	45,853.09	45,853.13	-	-	-
Ammonia Nitrogen	g N/m ³	231,035.00	4.00	5.60	0.01	0.01	0.00
Soluble TKN	g N/m ³	231,035.00	4.00	5.60	0.01	0.01	0.00
TKN	g N/m ³	231,035.00	4.00	5.60	33.21	38.03	38.03
TN	g N/m ³	231,035.00	4.00	5.60	33.21	38.03	38.03
	kg/d	67.00	167.50	234.50	-	-	-
Ortho-Phosphate	g P/m ³	0.00	5.70	5.70	0.23	0.20	0.20
TP	g P/m ³	0.00	5.70	5.70	49.61	56.96	56.96
	kg/d	0.00	238.69	238.69	-	-	-
Dissolved Oxygen	g O ₂ /m ³	0.00	0.00	0.00	0.58	0.65	2.31
Alkalinity	g CaCO ₃ /m ³	350.00	350.00	350.00	436.15	446.02	469.46

Table 53 - Simulation Results - streams characterisation on the 80th day of the simulation - Part II.

		ml(4)	ml(5)	ml(6)	ml(7)	ml(8)	ml
Flow	m ³ /d	-	-	-	-	-	102,855.54
TSS	g/m ³	3,157.21	3,160.17	3,163.19	3,163.75	3,153.95	3,153.95
	kg/d	-	-	-	-	-	324,401.38
VSS	g/m ³	1,862.56	1,865.60	1,868.70	1,869.23	1,858.97	1,858.97
Soluble BOD₅	g O ₂ /m ³	61.88	40.05	18.17	0.41	0.16	0.16
BOD₅	g O ₂ /m ³	347.71	325.81	303.91	283.65	270.50	270.50
Soluble COD	g COD/m ³	345.60	312.54	279.39	252.48	252.09	252.09
COD	g COD/m ³	3,102.19	3,073.62	3,045.06	3,018.93	3,003.36	3,003.36
	kg/d	-	-	-	-	-	308,911.96
Ammonia Nitrogen	g N/m ³	0.00	0.00	0.01	0.33	2.05	2.05
Soluble TKN	g N/m ³	0.00	0.00	0.01	0.33	2.05	2.05
TKN	g N/m ³	38.03	38.03	38.03	38.03	38.03	38.03
TN	g N/m ³	38.03	38.03	38.03	38.03	38.03	38.03
	kg/d	-	-	-	-	-	3,911.58
Ortho-Phosphate	g P/m ³	0.20	0.20	0.21	0.21	0.21	0.21
TP	g P/m ³	56.95	56.95	56.95	56.94	56.94	56.94
	kg/d	-	-	-	-	-	5,856.54
Dissolved Oxygen	g O ₂ /m ³	3.17	3.16	3.07	3.43	3.74	3.74
Alkalinity	g CaCO ₃ /m ³	493.33	513.19	529.44	541.09	547.35	547.35

Table 54 - Simulation Results - streams characterisation on the 80th day of the simulation - Part III.

		ml1/ml2	eff1/2	exc1/2	recirc1/2	eff	exc
Flow	m ³ /d	51,427.77	20,861.18	1,242.43	29,324.16	41,722.36	2,484.86
TSS	g/m ³	3,153.95	12.42	5,297.89	5,297.89	12.42	5,297.89
	kg/d	162,200.69	259.12	6,582.26	155,356.05	518.24	13,164.53
VSS	g/m ³	1,858.97	7.32	3,122.62	3,122.62	7.32	3,122.62
Soluble BOD₅	g O ₂ /m ³	0.16	0.16	0.16	0.16	0.16	0.16
BOD₅	g O ₂ /m ³	270.50	1.22	454.27	454.27	1.22	454.27
Soluble COD	g COD/m ³	252.09	252.09	252.09	252.09	252.09	252.09
COD	g COD/m ³	3,003.36	262.92	4,873.56	4,873.56	262.92	4,873.56
	kg/d	154,455.98	5,484.89	6,055.07	142,913.17	10,969.79	12,110.14
Ammonia Nitrogen	g N/m ³	2.05	2.05	2.05	2.05	2.05	2.05
Soluble TKN	g N/m ³	2.05	2.05	2.05	2.05	2.05	2.05
TKN	g N/m ³	38.03	2.20	62.48	62.48	2.20	62.48
TN	g N/m ³	38.03	2.20	62.48	62.48	2.20	62.48
	kg/d	1,955.79	45.80	77.63	1,832.32	91.61	155.27
Ortho-Phosphate	g P/m ³	0.21	0.21	0.21	0.21	0.21	0.21
TP	g P/m ³	56.94	2.19	94.30	94.30	2.19	94.30
	kg/d	2,928.27	45.75	117.16	2,765.30	91.50	234.33
Dissolved Oxygen	g O ₂ /m ³	3.74	3.74	0.00	0.00	3.74	0.00
Alkalinity	g CaCO ₃ /m ³	547.35	547.35	547.35	547.35	547.35	547.35

Table 55 - Simulation Results - streams characterisation on the 80th day of the simulation - Part IV.

		overflow	sludge0	filtrate	sludge
Flow	m ³ /d	1,240.70	1,244.16	1,091.26	152.90
TSS	g/m ³	79.47	10,501.81	525.09	81,706.47
	kg/d	98.60	13,065.93	573.01	12,492.92
VSS	g/m ³	46.84	6,189.85	309.49	48,158.48
Soluble BOD₅	g O ₂ /m ³	0.16	0.16	0.16	0.16
BOD₅	g O ₂ /m ³	6.97	900.32	45.17	7,003.66
Soluble COD	g COD/m ³	252.09	252.09	252.09	252.09
COD	g COD/m ³	321.41	9,413.07	710.14	71,526.65
	kg/d	398.78	11,711.37	774.94	10,936.42
Ammonia Nitrogen	g N/m ³	2.05	2.05	2.05	2.05
Soluble TKN	g N/m ³	2.05	2.05	2.05	2.05
TKN	g N/m ³	2.96	121.84	8.04	934.05
TN	g N/m ³	2.96	121.84	8.04	934.05
	kg/d	3.67	151.59	8.78	142.82
Ortho-Phosphate	g P/m ³	0.21	0.21	0.21	0.21
TP	g P/m ³	3.36	184.99	11.13	1,425.85
	kg/d	4.17	230.15	12.14	218.01
Dissolved Oxygen	g O ₂ /m ³	0.00	0.00	0.00	0.00
Alkalinity	g CaCO ₃ /m ³	547.35	547.35	547.35	547.35